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SEEKING LOW ICE ADHESION

John M. Sayward

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) ➤ Icing impairs operation of helicopters and other aircraft, antennae, power and communication lines, shipping and superstructures, canal locks, etc. Prevention or easier removal of icing requires reduction of its adhesion strength. Literature study shows that adhesion results from secondary (van der Waals) forces yet exceeds normal cohesive strengths. It depends on free surface energy, low contact angle, good contact and wetting, cleanliness, and texture. Modes of adhesion testing are briefly discussed. Poor adhesion occurs with low energy surfaces or contaminants, e.g. hydrocarbons, fluorocarbons, waxes, oils, etc., particularly when textured or porous. The resulting low contact angle, poor wetting and occlusion of air at the interface weaken the bond or provide stress loci which can initiate			

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20. Abstract (cont'd).

→ cracks and failure. Coefficient of expansion differences may help in release of ice. Further ideas appear among the 100 abstracts presented. A survey of over 300 manufacturers produced over 100 replies. Half of them offered some 100 products deemed worth testing. These are listed with addresses and contacts. Besides simple resins and other release agents, they include composites which combine low surface energy and stronger materials as micro-mixture, interpenetrating-network, "plastic-alloy," or filler-matrix systems. About 15 to 20 products appear of special interest. Samples of liquid coating or supplier-prepared panels of many are available for the testing phase to follow.

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ii

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PREFACE

This report was prepared by John M. Sayward, Research Chemist, of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by DA Project 4A762730AT42, *Design, Construction and Operations Technology for Cold Regions*, Technical Area 04, *Environmental Constraints on Materiel Development*, Technical Effort E1, *Environmental Control Methods*, Work Unit 001, *Prevention and Control of Ice Adhesion*.

The author wishes to thank Dr George Ashton for guidance in conducting this research, L David Minsk for sharing of his files and technical review of this report, and Stephen Ackley for also technically reviewing this report

Notes and correspondence not included herein have been retained. In Notebook D-0008 are recorded notes and ideas that bear on ice adhesion and its control and removal

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2523-2524

2525-2526

2527-2528

2529-2530

2531-2532

2533-2534

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CONTENTS

	Page
Abstract	i
Preface	iii
Introduction	1
Objectives	1
Adhesion and the interface	1
Forces	2
Wetting, roughness and air	3
Contact angle, θ	3
Critical surface tension γ_c	5
Lowering ice adhesion	5
Liquid-like layer	10
Teflon PTFE ice adhesion	10
Resilience	10
Flotation and adhesion	10
Waterproofing in nature	11
Adhesion testing	12
Discussion	12
How to obtain low ice adhesion?	12
Air at the interface	14
Survey of manufacturers	15
Highlighted products	16
Comments	16
Literature survey	16
Chemical abstracts	16
Other literature	18
Conclusions and recommendations	18
Literature cited	19
Appendix A. Adhesion testing	21
Appendix B. Listing of commercial products	31
Appendix C. Manufacturers' addresses and contacts	49
Appendix D. Chemical abstracts	57

ILLUSTRATIONS

Figure	
1 Cohesion-adhesion work $W = \gamma A$, $\Sigma W = 2\gamma A$	2
2 Effect of surface texture on adhesion	4
3 Contact angles and force diagrams	4
4 Measurement of contact angle	6
5 Flotation	11
6 Waterproofing	12

TABLES

Table	
1 Values of γ_c for some low energy polymer and surface components	6
2 Critical surface tension of polymers	8

SEEKING LOW ICE ADHESION

John M. Sayward

INTRODUCTION

Broadly speaking, icing is the deposition of frozen water on surfaces at or below freezing. It may result from rain, freezing rain, sleet, wet snow, fog, supercooled clouds or vapor, or from spray or splashing water. Even above-freezing wet snow may, in some instances, stick to surfaces. As man's activities have broadened and become more sophisticated, icing has become troublesome. It is especially hazardous to aircraft (notably on helicopter blades). It also affects power and communications lines (directly or by ice-broken trees), antennas, ships, walls of canal locks, pavements, etc.

Where icing can't be tolerated, costly means are needed to prevent or remove it. Control of ice by physical removal (by heating or chemicals) may be possible but is expensive and not broadly practicable.

OBJECTIVES

The objective here is to learn what causes ice adhesion and how to minimize it, drawing on adhesion, wettability and interface chemistry

From this base and from specialized literature on ice adhesion, testing and countermeasures experience, means are sought for reducing the adhesion of ice so that it will self-shed or be easier to remove mechanically. Also sought in this study are commercial products of interest for tests of ice adhesion strength.

ADHESION AND THE INTERFACE

Crucial in icing is the substrate/ice interface, its chemistry and physics. Could these be modified so as to repel ice? Complete repulsion, zero ice adhesion bond strength, is unattainable because all matter exhibits some degree of mutual attraction, e.g. between liquid and solid in contact (Adam 1963, Zisman 1964). That reduced adhesion is attainable, however, is well known in adhesion technology. Alteration of the interface, as by dirt, dust, grease or moisture, or poor contact, can impair bonding. The chemical nature of the materials is also a factor (Eley 1961). In this section, interface chemistry and forces, contact angle and wetting are discussed in relation to adhesion and abhesion (release or parting).

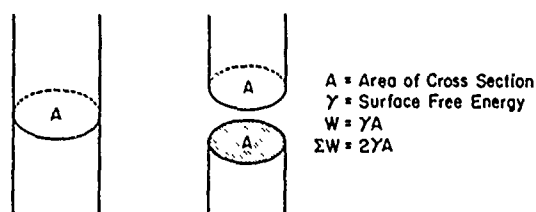


Figure 1. Cohesion-adhesion work $W = \gamma A$, $\Sigma W = 2\gamma A$.

Any system is most stable when its free energy is at a minimum. A mixture of hydrogen and oxygen is only quasi-stable—a spark or flame induces a reaction evolving energy (heat); the water formed is more stable. The reverse reaction requires application of energy—heat or electricity—to dissociate water to its components. Adhesion is similar. When two surfaces come together, residual surface forces interact, releasing energy. Conversely, it takes energy to create new surfaces, as by pulling apart adhered joints (Fig. 1) (Gregg 1961).

The surface free energy arises from imbalance between the interior, where intermolecular forces are mutually satisfied among neighbors, and the exterior, where lack of neighbors leaves some unsatisfied. This leads molecules to seek the interior, minimizing the surface energy and area. Thus a blob of liquid tends to form a spherical drop, the form with a minimum area/volume ratio, and hence minimum surface free energy. The surface free energy γ in mJ m^{-2} (ergs cm^{-2}) results from the residual unsatisfied forces remaining in a surface. This drawing together of molecules (as though enclosed in an elastic sheath) produces an apparent surface tensile force called surface tension. This is also designated γ (mN m^{-1}) (dynes cm^{-1}), and is the same numerically and dimensionally as surface free energy.

Referring to Figure 1, when a body is separated into two parts, the work to create the two new surfaces is

$$\Sigma W = 2\gamma A$$

where A is the area of the cross section. When the two are again brought together, such energy is released as surface forces become mutually satisfied. This is the work of cohesion for a homogeneous material, or of adhesion for

dissimilar halves or with an adhesive film between. Satisfaction of forces is incomplete when contamination is present, when contact is not intimate, or when one surface has "low energy," i.e. is so self-satisfied that there is little attraction for neighboring material.

Forces

What are the forces involved in adhesion? Rarely are they primary chemical bonding (valence) forces, which are ionic-electrostatic or homopolar (electron-sharing). These are effective only at typical bond lengths of 0.15-0.2 nm (1.5-2 Å) and decrease rapidly with distance.

Adhesion generally involves secondary attractive forces (Salomon 1965). These are the van der Waals forces (London dispersion and Debye induction effects), believed a consequence of the negative electron cloud relative to the positive nucleus of the atom. They involve energies of 8.4-16.8 MJ kg-mol^{-1} (2-4 kcal mol^{-1}) vs 42-420 MJ kg-mol^{-1} for primary bonds. Though most effective at about 0.3-0.50 nm, the van der Waals forces have some effect at considerably greater distances. Even at 10 nm they may be 98 kPa (1 kgf cm^{-2} or 1 atm) increasing exponentially at closer range; they have been estimated at 5 nm or less to be strong enough (ca. 30 MPa or 300 kgf cm^{-2}) to account for good adhesive bonding.

Typically, good adhesive joints result from adhesive-adherend interaction at much larger than interatomic distances. They have perhaps one-tenth the theoretical strength based on the forces available at the interface (Dunning 1961, Adamson 1967), due presumably to imperfect matching, contamination, and non-perfect intimacy of contact.

Also likely involved in ice adhesion is hydrogen bonding. This is an electrostatic interaction resulting from the sharing of a proton (hydrogen atom) between two electronegative atoms (Glasstone and Lewis 1960). The latter must be small, e.g. F, N, or most commonly O. H-bonding holds water molecules together in random clusters in the liquid and binds them into the rigid crystal lattice of ice (Kamb 1972).

H-bond energies, 8.4-42 MJ kg-mol^{-1} (2-10 kcal mol^{-1}) (Pauling 1960), are comparable with the weaker primary bonds and generally exceed the van der Waals attraction (Salomon 1965). Their range of action extends beyond the latter but has greatest effectiveness at comparable distances, 0.1-0.5 nm (1-5 Å). The ability of optical flats or gage blocks to adhere when closely

pressed or wrung together is evidence of interfacial forces effective well beyond atomic distances.

Wetting, roughness and air

The ability of one material or an applied adhesive layer to "wet" or thoroughly spread as a fluid on another (substrate) material (Zisman 1964, Huntsberger 1964) is important to good adhesion in aiding trans-interface transfer of forces. For a solid adhesive, this can be brought about by heating or use of a solvent, as heat or solvent escapes, the adhesive sets. Or, a liquid system may be solidified by polymerization, induced chemically and/or by heat or catalyst. Ice is an adhesive of the first type.

Physical roughness plays only a secondary role in adhesion. Where wetting is good, roughness can enhance adhesion by increasing the contact area for exchange of forces as well as by "tooth" effects. Conversely, roughness may increase the chance of retention of air (Salomon 1965) or other contamination, e.g. dust or oil, and hence can further impair wetting and adhesion. The effect of roughness on wettability is discussed below in connection with contact angle.

Interface contamination or imperfections affect adhesion (Adamson 1967, Salomon 1965, Zisman 1964). Contaminants interrupt the trans interface exchange of forces.

An important contaminant in adhesion is air. When wetting is incomplete, pockets of air are left in hollows or adhering to the surface, reducing bonding. Such pockets also can be loci of stress concentrations, with consequent initiation or propagation of adhesive failure. This is the more true for smooth surfaces, where coplanarity of contaminant patches aids propagation of failure cracks. Conversely, by interrupting such coplanarity a rough surface can minimize contaminant effects, as shown in Figure 2. Since good wetting is a necessity for good adhesion, poor wetting and occlusion of air may be a way to bring about poor adhesion of ice.

Wetting depends on the attraction between applied liquid and solid (Zisman 1964), i.e. on secondary and H-bonding forces, which the surface energy γ reflects. For hard solids γ is 500-5000 mJ m⁻² (500-5000 ergs cm⁻²), increasing with hardness and melting point, e.g. metals, oxides, nitrides, sulfides, silica, ruby, diamond. For soft organic solids generally γ is less than 0.1 mJ

m⁻² (ergs cm⁻²), e.g. waxes, polymers, most organic compounds. For liquids (excluding liquid metals), γ is also less than 100 mJ m⁻². Low energy liquids, i.e. most organics (typical γ of 20-40 mJ m⁻²), creep over and wet solids readily because their internal forces are not strong, as evidenced by their boiling points being lower than those for higher energy liquids. Water, with $\gamma = 72$ mJ m⁻² (72 ergs cm⁻²), is one of the latter, owing to the role of H-bonds in holding it together. So is mercury, in which metallic bonding does this. Added detergents (wetting agents) improve wetting by water, by lowering its surface tension (Zisman 1964); this also increases the adhesive and lowers the cohesive strength of ice (Salomon 1965, citing Bowden and Tabor).

For the substrate it works the other way. If its surface energy is high, as for metals, oxides and inorganics in general, the residual attractive forces are significant (Zisman 1964). Practically any liquid will spread on high energy surfaces, and they are therefore hard to keep clean.

If surface energy is low, as for waxes and many polymers, self-satisfied forces provide little inducement for liquids to spread. It is to this type we must look for low ice adhesion. Although the surface energy (or tension) of solids is not as readily measured as for liquids, values are obtainable by analogy with the liquid phase, by specialized measurements (Adamson 1967, Dunning 1961), from contact angles (see below) or calorimetric heat of solution or other thermodynamic considerations.

Contact angle, θ

Wettability is assessed by the contact angle θ formed by liquid and substrate. Values of θ vary inversely with mutual attraction and ease of wetting and can range from 0° to well over 90° (theoretically to 180°). Figure 3 shows θ for wetting and non-wetting liquids in a tube and for typical drops, with the associated force diagram. At the triple intersection of the solid, liquid (or second solid) and vapor surfaces in equilibrium, surface tension forces are balanced (subscripts S, L, V signify solid, liquid, vapor):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

which may be rearranged as

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \quad (2)$$

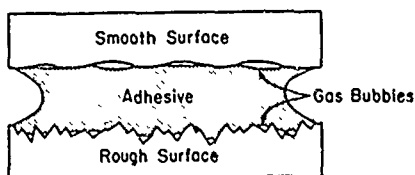


Figure 2. Effect of surface texture on adhesion. Co-planarity of occluded bubbles, as on smooth surface, weakens joint. Interruption of co-planarity, as on rougher surface, strengthens joint.

Meanwhile, the work of adhesion may be expressed (Salomon 1965) as

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (3)$$

Substituting from eq 2,

$$\begin{aligned} W_A &= \gamma_{LV} + \gamma_{LV} \cos \theta \\ &= \gamma_{LV} (1 + \cos \theta). \end{aligned} \quad (4)$$

Equation 1 is Young's equation, eq 3 the Dupré equation, and eq 4 may be called the Young-Dupré equation. Whereas γ_{SV} and γ_{SL} are difficult to determine in eq 1, 2 or 3, the variables on the right in eq 4 are easily measured.

High wettability means high work of adhesion. Equation 4 shows how work of adhesion (and hence wettability) relate to θ :

$\theta = 0^\circ$	$\cos \theta = 1$	$W_A = 2\gamma_{LV}$	complete wetting, good adhesion
90°	0	γ_{LV}	poor wetting and adhesion
180°	-1	0	no wetting and adhesion

In reality, the third case does not exist (Zisman 1964, Adam 1963), since there is always some residual attraction between two materials due to van der Waals forces, and always some adhesion. Actually, γ may be found to be as large as 110° - 115° for water (on waxy or $-\text{CH}_3$ surfaces; Adam 1963, Osment 1963), or as large as 154° for mercury on steel (Davies and Rideal 1961).

Roughness of surface can affect θ (Zisman 1964, Adamson 1967, Zettlemoyer 1968), decreasing it when θ is less than 90° , and increasing it when θ is greater than 90° . Thus, on rough wax θ is increased to 132° (Davies and Rideal 1961).

Values of θ are also increased on open-structure, fine perforated surfaces, where a high θ prevents penetration of small openings (Salomon 1965, Warburton 1963, Adam 1963). This lowers the apparent surface energy at the interface, since the liquid is only partly in contact with the solid, and partly with air (which in effect is not "wetted"). This effect is seen on fine-screen, porous solids and fabrics that are hydrophobic (water-repellent). Thus wetting and adhesion of water are reduced and the material is made more waterproof than without perforations. Similar effects account for water repellency in nature (Warburton 1963, Crisp 1963).

Contact angles may be judged within 10 - 15°

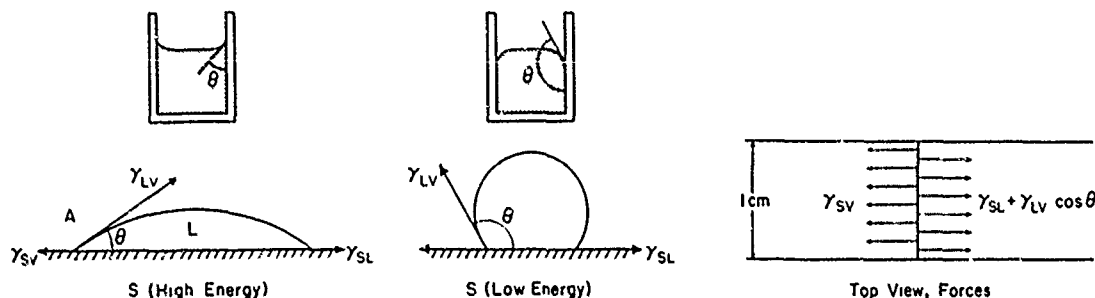


Figure 3. Contact angles and force diagrams. (After Salomon 1965, Gregg 1961).

by eye (Adam 1963). Measurement of θ is usually made as shown in Figure 4 (Adamson 1967, Davies and Rideal 1961).

In Figure 4a a slab of solid is partially immersed and its angle adjusted until the liquid touching it remains horizontal (no meniscus) on one side. When $\theta < 90^\circ$, this condition may be judged from the side, or perhaps more easily by looking down from the top and noting the reflective surface. For $\theta > 90^\circ$, the slab prevents viewing from above, and the judgment must be made from the side. Preferably, the test is made in a tank completely filled, so that the surface rests above the plane of the water-repellent sides.

In Figures 4b and 4c θ is measured as a sessile drop or air bubble rests on the test surface, using a microscope with goniometer. In all cases, the angle is measured as shown, on the liquid side of the intercept.

Misleading contact angles can be had without care as to cleaning the surface, avoiding contamination, and attaining equilibrium (or comparing advancing and receding values, which are particularly likely to differ if there be contamination or roughness). Method (a) may be simpler but involves larger specimens and liquid volume and more chance of contamination than drop or bubble methods; it may handle the advancing vs receding observations more easily, however.

Critical surface tension γ_c

A useful concept in considering contact angle, wettability and adhesion is the critical surface tension γ_c (Zisman 1964). For a given substrate, this is determined by measuring θ with a series of similar liquids of different γ . Graphing $\cos \theta$ vs γ gives a linear plot, extrapolation of this to $\cos \theta = 1$ (i.e. $\theta = 0$) shows the value γ_c for which wetting theoretically would be complete.

To spread on a given substrate, a liquid must have $\gamma < \gamma_c$. This approach is most useful for low energy surfaces of $\gamma < 30 \text{ mJ m}^{-2}$ (30 ergs cm^{-2}). Deviations of such plots from linearity are more likely for values of $\gamma > 50$, i.e. for liquids of high energy, since they are always of the H-bonding type.

Values of γ_c are useful for evaluating the wettabilities of low energy surfaces. Thus, for a monolayer anchored to a substrate by polar groups (acid, alcohol, ester), wettability is governed by the end groups exposed ($-\text{CH}_3$, $-\text{CHF}_2$, $-\text{C}_6\text{H}_5$, etc.) and decreases for substituents,

on an organic carbon chain substance, in the order $\text{N} > \text{O} > \text{Cl} > \text{H} > \text{F}$ (Salomon 1965). γ_c is useful for comparing the wettabilities of low energy polymer surfaces, decreasing as shown for the following structures (Zisman 1964):

	HCl	HCl	HH	HF	HF	FF	FF
	-C-C-	-C-C-	-C-C-	-C-C-	-C-C-	-C-C-	-C-C-
$\gamma_c =$	HCl	HH	HH	HH	HF	HF	FF
(mJ m ⁻²)	40	39	31	28	25	22	18

The lowest value known is $\gamma_c = 6 \text{ mJ m}^{-2}$, for a condensed monolayer of perfluoric acid, $\text{F}_3\text{C}(\text{CF}_2)_9\text{COOH}$, the most nonwettable surface ever reported (Zisman 1964); every liquid studied was unable to spread on it. The lowest for any solid polymer is $\gamma_c = 10.6 \text{ mJ m}^{-2}$, for polymerized methacrylic ester of perfluoro-octanol, $\text{CH}_2 = \text{CHC}(\text{O}(\text{C}_8\text{F}_{17}))\text{CH}_2$.

As they may be of some guidance in seeking surfaces with high θ , low wettability and low ice adhesion, values of γ_c for a number of low energy polymer surfaces are shown in Table 1 (Zisman 1964). A further listing of γ_c for polymers (both are from the Naval Research Laboratory) appears in Table 2 (Shafirin 1967).

Lowering ice adhesion

To reduce the adhesion of ice (an adhesive whose liquid form is water), requires reducing substrate wettability, making it more hydrophobic. This implies reducing its reactivity and surface forces, making it more inert, more incompatible with water. The resulting higher contact angle makes it more likely to occlude air at the interface.

Water is prone to hydrogen bonding, which is the basis of the ice structure, and thus water and ice are attracted to a substrate having H-bondable components, i.e. oxygen atoms. A low ice adhesion surface should, then, be free of oxygen atoms, or have them well screened by more inert atoms and groups. While capable of H-bonding in other situations, H as in hydrocarbons (Glasstone and Lewis 1960) and also F as in fluorocarbons (Pauling 1960) have been stated to not H-bond, although Eley (1961) does suggest that even F in F-C bonds can exhibit some H-bonding.

Chemical bonding strength or energy varies with different atom pairs and with what may be attached to them. It thus contributes to the relative activity or inertness of a substrate. A

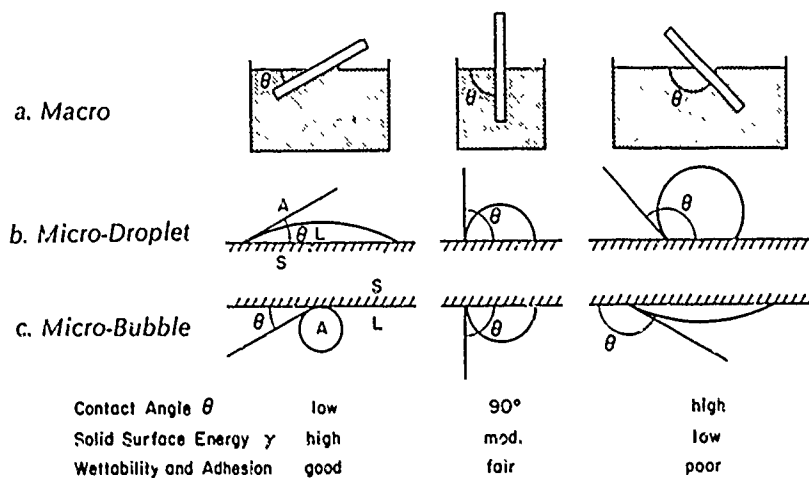


Figure 4. Measurement of contact angle.

Table 1. Values of γ_c for some low energy polymer and surface components (Zisman 1964).

Polymer of		γ^*
-methacrylic ester of perfluoro-octanol	$\left[\begin{array}{c} \text{H} \text{ CH}_3 \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \text{ CO}(\text{CF}_2)_7\text{CF}_3 \end{array} \right]_n$	10.6
-hexafluoropropylene	$\left[\begin{array}{c} \text{F} \text{ F} \text{ F} \\ \quad \quad \\ -\text{C}-\text{C}-\text{C}- \\ \quad \quad \\ \text{F} \text{ F} \text{ F} \end{array} \right]_n$	16.2
-tetrafluoroethylene (PTFE)	$\left[\begin{array}{c} \text{F} \text{ F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \text{ F} \end{array} \right]_n$	18.5
-trifluoroethylene	$\left[\begin{array}{c} \text{F} \text{ F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \text{ F} \end{array} \right]_n$	22
-(vinylidene fluoride)	$\left[\begin{array}{c} \text{H} \text{ F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \text{ F} \end{array} \right]_n$	25
-(vinyl fluoride)	$\left[\begin{array}{c} \text{H} \text{ F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \text{ H} \end{array} \right]_n$	28
-ethylene (PE)	$\left[\begin{array}{c} \text{H} \text{ H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \text{ H} \end{array} \right]_n$	31
-trifluorochloroethylene	$\left[\begin{array}{c} \text{F} \text{ Cl} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \text{ F} \end{array} \right]_n$	31
-styrene	$\left[\begin{array}{c} \text{H} \text{ H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \end{array} \right]_n$	33

* γ , in mJ m^{-2} = dynes cm^{-1} ; or mJ m^{-2} = ergs cm^{-2} .

Table 1 (cont'd).

Polymer of		γ^*
-(vinyl alcohol) \longrightarrow	$\left[\begin{array}{c} \text{H OH} \\ -\text{C}-\text{C}- \\ \text{H H} \end{array} \right]_n$	37
-(ethyl methacrylate) \longrightarrow	$\left[\begin{array}{c} \text{H CH}_3 \\ -\text{C}-\text{C}- \\ \text{H C-OCH}_3 \\ \\ \text{O} \end{array} \right]_n$	39
-(vinyl chloride) \longrightarrow	$\left[\begin{array}{c} \text{H Cl} \\ -\text{C}-\text{C}- \\ \text{H H} \end{array} \right]_n$	39
-(vinylidene chloride) \longrightarrow	$\left[\begin{array}{c} \text{H Cl} \\ -\text{C}-\text{C}- \\ \text{H Cl} \end{array} \right]_n$	40
-(ethylene terephthalate) \longrightarrow	$\left[-\text{O}(\text{CH}_2)_2 \text{OC} \begin{array}{c} \text{O} \\ \diagup \diagdown \\ \text{C} \end{array} \text{C} \begin{array}{c} \text{O} \\ \diagdown \diagup \\ \text{C} \end{array} \right]_n$	43
-(hexamethylene adipamide) (nylon 6/6) \longrightarrow	$\left[\begin{array}{c} \text{H} \quad \text{H O} \\ -\text{N}(\text{CH}_2)_6 \text{N}-\text{C}-(\text{CH}_2)_4 \text{C}- \\ \quad \\ \text{O} \quad \text{O} \end{array} \right]_n$	46

* γ in mJ m^{-1} = dynes cm^{-1} ; or mJ m^{-2} = ergs cm^{-2}

Surface constitution

A Fluorocarbon	γ^*	B Hydrocarbon	γ^*
$\cdot\text{CF}_3$	6	$\cdot\text{CH}_3$ (crystal)	22
$\cdot\text{CF}_2\text{H}$	15	$\cdot\text{CH}_3$ (monolayer)	24
$\cdot\text{CF}_2$ and $\cdot\text{CF}_2\cdot$	17	$\cdot\text{CH}_2$	31
$\cdot\text{CF}_2$	18	$\cdot\text{CH}_2$ and $\cdot\text{CH}$	33
$\cdot\text{CH}_2\text{CF}_2$	20	$\cdot\text{CH}$	35
$\cdot\text{CF}_2\text{CH}_2\cdot$	22		
$\cdot\text{CF}_2\text{CH}_2$	25	C Chlorocarbon	
$\cdot\text{CHCH}_2$	28	$\cdot\text{CCl}(\text{H})\text{CH}_2$	39
		$\cdot\text{CCl}_2\text{CH}_2$	40
		$\cdot\text{CCl}_3$	43

* γ in mJ m^{-1} = dynes cm^{-1} ; or mJ m^{-2} = ergs cm^{-2}

high energy surface, exhibiting high interfacial energy, has high attraction for a contacting fluid and a low energy surface the opposite. A low energy surface is relatively inert, its residual forces being more self-satisfied. This reflects both the intensity of bond energies and the size of atoms involved.

Polymeric fluorocarbons and hydrocarbons have low energy surfaces, because the C-F bond is the strongest involving single-bonded carbon, and the C-H bond energy is high. For C-F, it is 442 MJ kg-mol^{-1} (105.4 kcal g-mol^{-1}), for C-H 414 MJ kg-mol^{-1} (Pauling 1960). Some other single-bond energies are C-Cl 329 MJ kg-mol^{-1} , C-O 352 MJ kg-mol^{-1} , C-N 292 MJ kg-mol^{-1} , O-H 463 MJ kg-mol^{-1} , and C-Br 276 MJ kg-mol^{-1} .

The above shows why surfaces of fluorocarbons and hydrocarbons are of low energy. They thus have low attraction for water and low ice adhesion, as for Teflon (i.e. PTFE, polytetrafluoroethylene) and polyethylene, and other organic polymers with such surfaces. Some other bonds are of still higher energy, but these are unlikely to appear alone or exposed, or they involve O and N. Where not screened, their ability to H-bond enhances their attraction for water and ice, as seen in epoxy and polyester resins.

The relatively low adhesion of silicones to ice (Bass and Porter 1963, Landy 1969, Millar 1970) is explained by structural characteristics which

Table 2. Critical surface tension of polymers (Shafrin 1967).

The critical surface tension for spreading (γ_c) defines the wettability of a solid surface by noting the lowest surface tension (γ_L) a liquid can have and still exhibit a contact angle (θ) greater than zero degrees on that solid. The constant is expressed in units of dynes per centimeter and the temperature is specified; the following values are based on measurements made at 20 to 25°C.

The value of γ_c for a given solid is determined by observing the spreading behavior and the angle θ of a series of liquids of decreasing γ_L . A rectilinear relation exists between cosine θ and γ_L ; the intercept of this line with the $\cos \theta = 1$ (i.e. $\theta = \text{zero}$) line gives a value of γ_c which is independent of the nature of the test liquid and is a parameter characteristic of the solid surface only

Polymer	Critical surface tension, γ_c (dynes cm ⁻¹)	Ref
<i>Polyolefine and vinyl polymers</i>		
Poly (chlorotrifluoroethylene)	31	1
Polyethylene	31	2
	11.5	3
Poly (hexafluoropropylene)	16.2-17.1	4
Polystyrene	33-35	5
	30-35	6
Poly (tetrafluoroethylene)	18.5	7
Poly (trifluoroethylene)	22	8
Poly (vinyl alcohol)	17	9
Poly (vinyl chloride)	19	8
Poly (vinyl fluoride)	28	8
Poly (vinylidene chloride)	40	8
Poly (vinylidene fluoride)	25	8
<i>Acrylic polymers</i>		
Polyacrylamide	35-40	6
Polyacrylate	35	10
Poly (1,1-dihydroperfluorooctyl methacrylate)	10.6	11
Poly (methyl methacrylate)	33-44	12
	39	6
Poly [2 (N-propylperfluorooctanesulfonamido) ethyl acrylate]	11.1	11
<i>Polyesters</i>		
Poly (ethylene terephthalate)	43	5
	42.5	3
<i>Polyamides</i>		
Poly (6 aminocaproic acid)	42	13
Poly (11 aminoundecanoic acid)	33	13
Poly (decamethylene sebacamide)	32	13
Poly (heptamethylene pimelamide)	43	13
Poly (hexamethylene adipamide)	46	5
Poly (octamethylene suberamide)	34	13
Poly (nonamethylene azelaamide)	36	13

Table 2 (cont'd).

Polymer	Critical surface tension, γ_c (dynes cm ⁻¹)	Ref.
<i>Other organic polymers, copolymers and resins</i>		
Polyamide-epichlorohydrin resin	52	10
Poly (tetrafluoro ethylene-co-chlorotrifluoro-ethylene)		
80/20	20	1
60/40	24	1
Poly (tetrafluoroethylene-co-ethylene)		
50/50	26-27	1
Poly (tetrafluoroethylene-co-hexafluoro-propylene)		
94/6	19.0	14
92/8	18.3	14
86/14	18.2	14
84/16	18	14
77/23	17.8	14
Poly (vinylidene chloride-co-acrylonitrile)		
80/20	38-44	6
91/9	38	3
Urea-formaldehyde resin	61	10
<i>Natural polymers</i>		
Amylopectin	35	9
Amylose	37	9
Casein	43	10
Cellulose (regenerated)	44	9
Starch	39	9
Wool	45	10
<i>Semorganic polymers</i>		
Poly (dimethyl siloxane)	24	15

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keen their oxygen atoms well screened by methyl groups. Meanwhile, the silicone oxygens may aid attachment of a silicone coating by H-bonding to an underlying substrate, making it more permanent than wax.

Liquid-like layer

Much evidence has accumulated that a liquid-like or transition layer exists on ice, at free surfaces and at interfaces with solids (Jellinek 1959, 1964, 1972; Adamson et al. 1970, and Kvlivdze et al. 1970, Mantovani and Valeri 1978). Since its thickness depends on temperature and the nature of the surface, the latter must also affect ice adhesion via this layer. This reinforces the belief that low ice adhesion can indeed be achieved by choice of suitable substrates.

Teflon PTFE ice adhesion

Compared with inorganics (metals, oxides), the adhesion of ice is lower on organic polymers (Eley 1961, Raraty and Tabor 1958, Salomon 1965), due to the inertness of the hydrocarbon or fluorocarbon composition. Some polymers having more complex aliphatic hydrocarbon or fluorocarbon chains may have more ice adhesion than others owing to attraction due to double bonds, aromatic rings, or H-bondable elements (mainly O and N).

Fluorocarbons generally have low ice adhesion. For Teflon PTFE, however, repeated freezing cycles or high droplet impact velocities produce stronger ice adhesion than expected. Why?

First, Teflon PTFE has such high melt viscosity that it has to be processed (from powder form) by sintering rather than melting, this results in microporosity (Schlanger and Titterton 1977). In cycled freezings (Salomon 1965), or even in first freezing with high velocity droplet impact, as on a helicopter blade (Stallabrass and Price 1963), water may penetrate enough into the pores to anchor the ice.

Second, the resulting soaking, i.e. penetration of water molecules among the fluorocarbon chains, as Adam (1964) suggests, may also lower θ , thus increasing wetting.

Or, third, the micro or sub-micro patches of air normally occluded at the interface owing to Teflon's poor wettability (Salomon 1965) may be removed (by solubility, mechanical sweeping or migration into pores) during repeated freeze-thaw cycles or by high velocity droplet impact. Thus the impaired interaction and reduced bonding strength due to such air are lost.

So, other polymers of appropriate structure, more truly meltable and less viscous, and/or non-porous, may have a more impermeable surface and hence lower ice adhesion.

Resilience

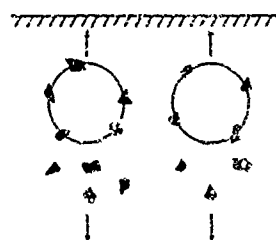
Another difficulty with low ice adhesion materials like polyethylene, Teflon or silicones is their softness or creep. Poor abrasion resistance may preclude their use on aircraft or wherever there is high impact and wear exposure. This may not be so much a drawback in some other icing situations, as with cables, antennas, ships, and canal locks. Such softness may be overcome in newer polymer formulations, composites or "plastic alloys" (Modern Plastics 1977, Arkles et al. 1974).

Rigidity or resilience may, however, affect adhered interface integrity. Flexible coatings have been noted to exhibit lower ice adhesion (Jellinek 1959, Stallabrass and Price 1963, Landy and Freiberger 1967 and 1968, Landy, undated and 1969). A degree of general flexibility can generate local stress and encourage crack initiation according to the Griffith-Irwin crack theory (Good 1972, in press). Rigidity may encourage propagation or failure once initiated, whereas local flexibility or toughness allows local "give" to discourage propagation.

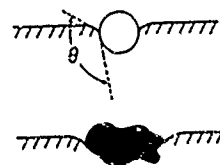
What seems needed for good adhesion is a form of toughness that will absorb stress without initiation or propagation of cracks. Conversely, then, to attain low ice adhesion we need a combination of rigidity and flexibility without elasticity at the interface. This is the basis of Sewell's (1971, 1974) flexible substrate idea, described later, and an earlier patent (Gaugler and Guenther 1948).

Flotation and adhesion

The flotation process for beneficiating low grade ores and separation of other finely divided materials also depends on contact angle and wetting. When air is beaten into a water dispersion of finely divided materials, differences in hydrophobicity, contact angle and wettability enable separation. Aided by additives (frothing agents, collectors, activators, depressants), the more hydrophobic components collect in the walls of air bubbles and may be skimmed off in the froth (Fig. 5). The more hydrophilic materials remain dispersed in the water. Thus valuable minerals can be separated from the "gangue" of low grade ores. In a sense, the frothed particles



a. Froth bubbles with non-wetted ore in flotation, while wetted gangue sinks.



b. Flotation of an individual particle.

Figure 5. Flotation.

are more readily "wetted" by air than by water.

Important as it is, flotation and the use of additives developed empirically. Only 60 years ago was the importance of contact angle θ recognized (Adamson 1967). Now the process and functions of additives are better understood, and electrical effects are also seen as a possible factor. In the preferential "attraction" of air to low energy hydrophobic interfaces, flotation is analogous to low ice adhesion through the concept of air attraction and occlusion at the interface, i.e. preferential "wetting" by air occurs in both.

Waterproofing in nature

Waterproofing is of interest because it, too, involves air/water/solid interaction and apparent preferential "wetting" by air. As Crisp (1963) describes, there are numerous examples of waterproofing in nature. These include insects which must have means of taking in air without drowning when immersed in rain or dew and yet also must conserve moisture in arid conditions, plants that need pores for air but also must conserve moisture when humidities are low, animals whose coats must remain dry to maintain thermal insulation, and birds whose water repellent feathers hold air for insulation to conserve body heat and also for preservation of buoyancy when on water. Closely perforated or hairy structures of hydrophobic character shed water or cause formation of a "gaseous plastron" by bird feathers, insects, leaves, etc. The plastron (shield

of occluded air) effect produces the silvery appearance often seen when leaves are immersed.

As stated previously, when θ is greater than 90° , it is larger on rough than on smooth surfaces (and conversely when θ is less than 90° , it is smaller on rough than on smooth). This can be rationalized on geometric grounds. A corollary is that a perforated or porous hydrophobic material that will not wet readily, i.e. a rough surface will also not wet nor allow liquid water to penetrate until a specific entry pressure is exceeded. This pressure is greater the finer the perforations and the greater the hydrophobicity. It derives from the greater θ on a rough surface.

Water spanning perforations is not wetting anything. As in the discussion of flotation (above), one may consider the substrate as preferentially "wetted" by air. So, surface tension forces tend to hold the meniscus in the perforations against appreciable pressure. Shown in Figure 6 (Zettlemoyer 1968) are cases of low θ (wettability) and high θ (waterproofing). Lowering the surface tension of the water as by adding a surfactant (wetting agent) lowers the θ and destroys the water resistance.

Man has found how to make fabrics water-repellent by utilizing similar techniques. Like the fibrils on plants and insects, the hairs on animals, and the interlocking parallel barbs on bird feathers, the fibers need to be in a compact and regular spacing and made hydrophobic, as by treatment with wax, silicone, or other hydrophobing agent. Not only fabrics but also

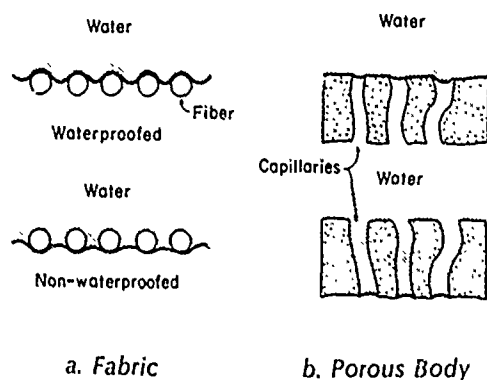


Figure 6. Waterproofing.

porous materials like leather, masonry, soils, etc., can be thus waterproofed. The non-wettability of the treated matrix, or its preferential "wetting" by air, aided by the relatively high surface tension of surfactant-free water, enables the repulsion of water. This is an objective, too, in seeking low ice adhesion.

Adhesion testing

Various methods are possible for ice adhesion testing, and a number of devices have been employed at different times and places. Variability among these due to idiosyncrasies of methods, procedures, conditions, materials, etc., makes it difficult to compare results. Ideally, then, given results should be compared with those on a common standard substrate, e.g. stainless steel, aluminum, or specified plastic, etc., tested in the same way. While the specifics of ice adhesion testing and apparatus used at CRREL will be considered elsewhere (Minsk, in preparation), some approaches and ideas concerning it are discussed briefly in Appendix A.

DISCUSSION

In essence, the geometry and especially the chemistry of the interface are critical in adhesion. Interface interaction may not be as expected when mere traces, even monomolecular layers, of extraneous contamination exist.

Hydrophobics, as from human skin, food, machinery, combustion fumes, industry, etc.,

can change a high energy surface to a poorly wetting one. Conversely, hydrophilics, e.g. dust, surfactants, water-soluble organics, may change a low energy to a wetting surface. Surface texture may influence interaction in either case—trapping contaminants and air, changing the contact angle, wetting and "tooth." Such factors are ever present in paint and adhesion technology. They are both a hope and a problem in weakening ice adhesion.

How to obtain low ice adhesion?

As is made clear above, conditions for low ice adhesion, i.e. abhesion, release or parting, may include:

1. Low energy surfaces of solid substrates (or applied coatings).
2. Absence of contamination of the surface by high energy materials or of the water by surfactant (surface tension reducing) substances.
3. Presence of contamination with even lower energy material to impair bonding across the interface and create consequent non-uniform stress distribution.
4. Occlusion of air at the interface to impair bonding and promote stress concentrations that can initiate or propagate adhesive cracks and failure.
5. An optimum degree of roughness-smoothness to encourage coplanar air entrapment and stress concentration and consequent initiation of cracks and their propagation to joint failure.
6. Appropriate substrate construction or properties that encourage generation and/or transmission of suitable stress and production of cracks for adhesive failure (i.e. self-shedding or easy removal of ice).
7. Appropriate stress (shock, flex, vibration, heat or thermal gradient) to induce loosening or failure.

These factors will be to varying degrees applicable in the several situations where low ice adhesion, self shedding or easy removal of ice is desired. Each will now be discussed.

1. Low energy surfaces

Low energy surfaces can be had by applying a wax (impermanent) or a monolayer of molecules of polar head/hydrophobic tail type (fatty acid, or ester alcohol). Though effective, such will be subject to wear. Better it is to make the object itself of low energy material or cover it with a macro coating (paint or film) of such material. This should be an organic polymer involving saturated (single bonded) carbon chains with only hydrogen and/or fluorine atoms on the carbons.

If other elements or atom groups, such as oxygen, nitrogen, carbon-carbon double bonds, acid, ketone, aldehyde, hydroxyl, amine, aromatic (benzene ring), etc., be present at all, they should be few in proportion and well screened by more inert components. Such may be the case with some silicones, which may be predominantly hydrocarbon chains, with their few oxygens situated internally and well screened.

Much of the information under *Adhesion and the Interface* points to fluorocarbons being superior to hydrocarbons for low ice adhesion. However, stronger ice adhesion to Teflon PTFE fluorocarbon upon droplet impact suggests that some fluorocarbons may not be the best, due perhaps to porosity. It might also signify some H-bonding with fluorine atoms on the carbon chain. Fluorine atoms can H-bond in other circumstances, and information is conflicting as to their doing so on a carbon chain. If this be so and if hydrogens on carbon are more restricted from H-bonding, a case might be made for hydrocarbons (as found in polyethylene, silicone, acrylic and some other polymers) being equally or more attractive for low ice adhesion.

2. Absence of high energy contamination

To avoid high energy materials on low energy substrates requires reasonable care in preparation. In subsequent use this may be problematical, depending on environmental and other factors. Likewise, the ice (water) should be free of surfactant material. However, one has to accept atmospheric moisture and contaminants as they are (although careful washing and rinsing of the substrate may eliminate residual natural or washing surfactants at the time of testing).

3. Presence of low energy contamination

This could include deliberate coating with waxes, oils, gums, etc., but such may be impermanent and hardly of value unless they result in

still lower energy than provided for in (1), or unless they have value through the creation of differential stress concentrations.

4. Occlusion of air

In the present view, this may be a most important factor in low ice adhesion. It appears to be governed primarily by the non-wetting, high θ , low γ_c and roughness-smoothness properties of the substrate/water system. It could be helpful in cases of relatively quiescent and bulk freezing but less likely for high velocity impinging droplets. Thus, on aircraft and particularly helicopter rotors, air may be forced away from the interface before freezing occurs there.

Conceivably, provision of a surface tending to adsorb and hold air as an adsorbed film would be of some benefit if the hydrophobic property be not affected. Conceivably, too, provision of a very slow, seeping flow of air from the interior through the surface might help weaken adhesion of the initial layer of ice in some of the applications, i.e. on lock walls and ship sides, if not on aircraft.

In the lock wall case, it might also help to inject highly atomized air, forming a cloud or layer of hyperfine bubbles next the wall at times when freeze-on is likely. Or, a similar effect might be had by release along the wall of a curtain of water saturated with air at high pressure. Occlusion of air may also be improved by surface geometry.

5. Optimum roughness-smoothness

How contamination of the adhesion interface, particularly with air, may affect adhesion-abhesion has been discussed. Roughness can provide "shelter" for contaminants or air, can affect θ and wetting, and can alter the co-planarity of stress concentrations arising at non-bonded contamination or air patches.

Roughness interlock may also enhance adhesion. So, in any given situation there may well be an optimum degree of roughness-smoothness for strong adhesion and another for low adhesion. Of these relationships there seems to have been little study. Since little is known and the conjecture is logical, this could bear careful study, drawing on modern methods of evaluating and controlling surface geometry.

6. Appropriate construction

To this point, provision for poor wetting, occlusion of air and loci of stress concentration have been suggested to make the ice-substrate

bond weak. How can stress be encouraged at the interface?

Some very good thinking is due to Sewell (1971) who developed the flexible substrate idea: a thin layer of sponge rubber topped by a thin, impervious, high modulus (flexible but not resilient) film which would have enough "give" to initiate a crack and enough rigidity (non-toughness) to help it propagate.

In any case, some external stress is needed or will help for cracking and ice shedding to occur. This could mean designing the member of material and cross-section such that it can flex and transmit resulting stress to the interface, or such that other sorts of stress can be conducted to the interface.

7. Appropriate stress

Stress suitable for initiating and propagating adhesive failure with the help of air occlusions and stress concentration loci at the interface might be generated in several ways.

- 1 Single shocks delivered to the member by direct mechanical impact or even through the adjacent air (on aircraft, wires, antennas, ship superstructures) or through the water (on lock walls or ship sides) as by hammer blow or explosive discharge.

- 2 Flexing of the member in normal use (helicopter blades, aircraft surfaces, wires and cables).

- 3 Sonic or ultrasonic vibration at optimum frequency imposed on the member electromechanically as needed

- 4 Heating (or cooling) the member (by conduction or possibly radiation) intermittently and briefly as needed, either overall or in alternate strips, to create temperature gradients and differential thermal expansion to stress the interface and initiate or propagate adhesive cracks

- 5 Providing alternating strips of high and low coefficient of expansion in or beneath the surface skin to develop stress upon temperature change

- 6 Utilizing bimetallic elements or strips* (metals of high and low coefficient of expansion

* Some manufacturers' information on these is at hand

laminated and formed so as to magnify displacement upon thermal change). Placed at intervals beneath a flexible surface skin, these could produce local stress upon heating, e.g. by radiation, electrical resistance, or piped hot fluid.

The coefficient of expansion concept has support from Landy and Freiberger (1968), who felt the difference in coefficient of thermal expansions of ice and substrate to be a factor in ice release, particularly for ice cooled considerably below its temperature of formation (0°C), a point also made by Mantovani and Valeri (1978).

All of the above would be followed by self-shedding or by manual or machine action to remove the loosened ice. Although the details of stresses (1-6) are not within the present scope, they may prove essential in achieving maximum effectiveness of any icephobic surface.

Air at the interface

When adhesion is poor, almost inevitably air must be occluded—mechanically trapped, held by contaminant, or left from incomplete wetting (e.g. Bascom et al. 1969). In a sense, a low energy surface may be considered to adsorb air or be preferentially "wetted" by air. Where would air come from at the interface?

The source of air at the ice/substrate interface may be:

- 1 Air held on the solid surface by adsorption.
- 2 Air incompletely displaced.
- 3 Air from internal pores of the solid, perhaps displaced by entry of water (such water kept from freezing by capillary forces)
- 4 Air mechanically entrained in the water about to freeze, as by splashing, atomizing, or lowering the pressure of water air-saturated under pressure
- 5 Air dissolved in the water, which is excluded upon freezing

Any of these might help to make an icephobic surface more effective

The possible significance of dissolved air is simply assessed here. The solubility of air is not great (17 m³/1000 m³ of water at 25°C), but it does increase as temperature decreases (29 m³/1000 m³ at 0°C). The solubility of air in ice is essentially nil, so that all air is rejected upon freezing. This accounts for the bubbly effect seen in rapidly frozen ice. When ice is slowly frozen, such air may be swept away or may form clouds or chains of bubbles, nucleated by foreign particles or by each bubble successively

If such excluded and occluded air be at the ice/substrate interface, how much might it reduce the area bonded?

Assuming that all air involved had been dissolved (none previously adsorbed on the solid surface), the air at 0°C in a layer of water only 0.3 nm (3 Å) (about one water molecule) thick would cover 2.7% of the surface one molecule thick (ca. 0.33 nm or 3.3 Å). If the dissolved air within the adjacent 10-molecule layer of water were to reach the interface before freezing was complete the air would cover 27% of the interface, if from 100 layers, the whole interface would be covered 2.7 molecules or nearly 1 nm (10 Å) thick.

The above suggests that dissolved air may indeed be a factor in low ice adhesion, given a low energy, poorly wetting surface. If air is, in effect, more attracted than water to such a surface, dissolved air might indeed be drawn to the interface from a layer a number of molecules thick before freezing to the surface is complete. Air adsorbed initially would augment the effect.

Some confirmation of this is seen in the NGASt (Naval, General and Air Staff Target) (1976) study. Adhesion was greatest for distilled water, least for melted rime. This might be expected, since rime formed by rapid freezing of tiny supercooled drops must contain much air from 1) air saturating the supercooled droplets and trapped as bubbles in ice upon exclusion during quick freezing, 2) adsorption of air on the large surface of many tiny and perhaps feathery crystals, 3) interstices among the particles (accounting for opaque white appearance and low density of rime). Depending on its history and handling, distilled water likely has less dissolved or emulsified air, and hence should bond more strongly upon freezing.

Since rime, from quick freezing of tiny supercooled droplets has occluded air (see above), it might be expected to adhere poorly, owing to the air present. However, discussion at the Rotary Wing Aircraft Symposium (Tolliver 1974) brought out that a silicone surface could shed glaze ice or clear ice but seemingly had little effect on rime ice. This might be explained as follows.

The particulate structure of rime should make it less rigid and brittle, and hence less prone to crack initiation and propagation. This may account for the better adherence of rime to a silicone surface. During the slower formation of

glaze or clear ice, some occluded air may be attracted to the silicone interface (which in effect is preferentially "wetted" by air), and the ice itself forms a more continuous and rigid structure. Here interface cracks could initiate and propagate more readily.

Abe et al. (1978) have developed a time-lapse film of rime accumulation on metal wires and on a flat "board," (shown by Kuroiwa at the recent Snow Removal and Ice Control Symposium sponsored by CRREL and the Transportation Research Board). Aggregates of rime were seen falling off occasionally. The substrate is understood to have been of vinyl plastic. This would seem to contradict Tolliver (1974) but may be a function of the particular conditions—water content of air, velocity, temperature, substrate, and flexing of aircraft surface in Tolliver's case (to which glaze ice would be more vulnerable than rime). Also, the falling rime may separate from itself more than from the substrate.

Other confirmation of the effect of air on ice adhesion is seen in observations of lower adhesion by droplet ice than by bulk frozen ice (except in the case of Teflon, where porosity allows impact penetration and anchoring of droplet ice) (Stallabrass and Price 1963, Landy undated).

In testing the adhesion of ice to low energy (air-attracting) materials, it would be of interest to compare results obtained with air-saturated water and with water completely free of dissolved air. In the latter case higher adhesion strengths would be anticipated. This would take some careful experiments with special provisions for complete exclusion of air.

In view of the above, it may be well in ice adhesion tests to use air saturated water rather than "de-aired" water. The latter may exhibit stronger adhesion than in real life where water is invariably air-saturated. The saturated water should give better reproducibility, too, since it is fixed, whereas the lower air content of "de-aired" water may vary with its history and handling. It may also be of interest to compare droplet and rime ice with ice frozen from bulk water, the former may contain more impurities adsorbed from the atmosphere.

SURVEY OF MANUFACTURERS

A survey of coatings, release agents, etc., available in industry, uncovered a number of

materials of interest for potentially low ice adhesion. Of some 300 firms surveyed, over 100 responded. About 100 products, from over 50 suppliers, appear to be of interest. Samples of coating material or supplier-prepared panels of many are at hand for the testing phase to follow.

Some products are composites, i.e. mixtures of other plastics or even inorganics as matrices or fillers or thoroughly intertwined—to give improved properties. Such micro-scale mixtures are "plastic alloys." Thus, the lubricity and water repellency of materials like Teflon may be retained while offering greatly improved hardness, durability and abrasion resistance. Some of these newer resins are of chemically modified or copolymer nature to make them harder and/or more impervious.

Materials found are listed in Appendix B. Based on chemical factors and properties given by suppliers, judgment of relative interest and suggested order of ice adhesion testing is indicated by the letters A, B, C and by a subsidiary 1, 2, and 3 within each group.

Although permanency of icephobic surfaces is desired, some are included even though impermanent. If highly effective and able to last at least an hour or so and be easily re-applied, such coatings could be of interest, for example, on helicopters (whose missions usually are short), if permanent types are not so effective or are difficult or expensive to apply. Impermanent types are generally down-rated, however.

Highlighted products

Highlighted below are the more interesting materials, mainly of the more permanent type. All are rated in the "A" class. Details of each are given in Appendix B, listed in alphabetical order by manufacturers' name to facilitate correlation with the company address listings in Appendix C.

CM-1 fluorocarbon copolymer (Allied Chemical Corp.)
 Celgard (Celanese Plastics Co.)
 Teflon/Kapton composite (Dielectrix Div., Carborundum Co.)
 DF-3200 (Dielectrix Div., Carborundum Co.)
 Polylube J (Custom Compounding)
 Debron 711 (deBeers Laboratories, Inc.)
 ARC (Abrasion Resistant Coating) (Dow-Corning Corp.)

R-4-3117 Conformal Coating (Dow-Corning Corp.)
 Teflon-P PFA Powder Coating (552-5010) (DuPont Co.)
 Teflon FEP Finish, 856-Line (DuPont Co.)
 Fluorocarbons and Combinations (Boyd Coatings Research, DuPont licensed applicator)
 Silicone-polycarbonate (PC) (General Electric Co., Plastics Dept.)
 Lectrofluor 405, now called Tufram PG-405 (General Magnaplate Corp.)
 Impax (Impact Plastics, Inc.)
 Vulkem 101 and 450 (Master Mechanics Co.)
 P/C Epoxy Teflon Coating TFE #4 (Peterson Chemical Co.)
 Ryton (Phillips Chemical Co.)
 Rilsan Nylon 11 (Rilsan Corp.)
 Silgan (SWS Silicones Co.)
 Porous Plastics (Springborn Laboratories, Inc.)
 Kro-Lon Surface (TFB, Inc.)
 Tullanox 500 (Tulco, Inc.)
 Tulcote 22 (Tulco, Inc.)
 Tullanox LC 410 (Tulco, Inc.)
 Tullanox formulations (Clifford W. Estes Co., formulator for Tulco, Inc.)
 Tullanox formulations (Silobond Products, Inc., formulator for Tulco, Inc.)
 Xylan Fluorocarbon Coatings (Whitford Corp.)
 (Several unique products) (Vitek Research)

Comments

Not all products listed here or in Appendix B may be suitable for the urgent helicopter blade situation. Some that are too erodable may well serve in other areas. Likewise are those specifically intended for use on porous materials like masonry and those available in sheet form. If sufficiently icephobic, these may be suitable on canal locks, for example. Some of the softer materials might do on wires and cables, where erosion is less and flexibility should aid ice shedding as they sway in the wind.

LITERATURE SURVEY

Chemical Abstracts

Chemical Abstracts was searched from early 1977 back to its initial issue (1907), developing 200-260 abstracts deemed of some interest in the

areas of ice adhesion, icing, anti-icing, de-icers, ice friction, "liquid-like layer" on ice and cloud physics (the genesis of icing problems). Some references are to patents, often for pavement, windshield or aircraft use. In general those involving ice melting by salts, solvents (alcohol, glycol) or heat are not of concern here. Little of significance appeared before 1931, while interest in icing increased considerably in the decades since WW II.

Abstracts of 100 of the more interesting and pertinent items appear in Appendix D. A few points from 22 that are striking and may be of particular use in developing means for low ice adhesion are set down here. These are included among 66 designated as of special interest by (X) in Appendix D. Numbers given (including superscripts) are the abstract references (P - patent); full references are given in Appendix D. Asterisks (*) mark those referenced in main text. Special comments are bracketed [].

- 28 5900* Surfactants make ice spongy [cf. 52, 5930', 82, 158151 P and Sayward 1963—effect of additives in snow].
- 37 697* Carbonated water makes softer ice.
- 40 4824² Silicones promising for low ice adhesion on rubber [cf. 43, 6860' P, 45, 10440' P].
- 42 2038* P *Propeller anti-ice coating with top layer less flexible than lower [cf. Sewell's flexible substrate, 78, 17171].
- 46 1674* P Ice adhesion reduced by surface organic-silicone formed in situ
- 47 1874' P Poly (monochlorotrifluoro ethylene) for low ice adhesion, also flexible.
- 52 5061* Metal amine complexes inhibit ice nucleation [cf. 83, 208580].
- 52 5930' Ice adhesion is lower for stainless steel and chrome than for steel and lower with surfactants in water, and is affected by roughness. [Being less subject to oxidation, stainless and chrome may have less surface oxide and consequent H-bonding tendency.]
- 55 15058* Receding rather than advancing contact angle more significant for adhesion of ice where drops are blown across surface, and

56 8089*

57 12661*

68 96849

71 102840 P

72 25378

72 123641

76 127910

78 17171

83 117065

83 117122

smooth surface better in this case for reducing adhesion. Ice nucleation is best near the isoelectric point of the solid nucleator, requires great supercooling for either (+) or (-) charged surface. [Perhaps on a charged surface drops might run off before freezing.] Epoxy resin with 80+ % of stainless steel particles filler resists rain, ice, etc. *Ice adhesion strength increases with area, freezing rate, water purity, age, stress application and lower temperature. Of 40 coatings a silicone was lowest. Silicone polymer salt lowers ice release to 6 psi from steel, < 3 psi from glass. Low ice adhesion to steel with monolayers or thin plastic coatings not correlated with contact angle but with air entrapment or cohesive failure of coating. Defective ice lattice near substrate signifies liquid-like layer. [cf. Discussion above and footnote on this abstract in Appendix D.] *Adhesive shear strength of ice relates to roughness and porosity and was found lower for silicone and polyimide than phenolic coatings having fluorinated fillers. Polyimide more durable than silicones. Polyethylene, polyvinyl chloride and Viniplasi had lowest ice adhesion of 10 plastics. *Thin sponge rubber on rigid base and with low energy surface film reduces ice adhesion, e.g. for helicopter blades (J.H. Sewell). Organosilicone epoxide coating greatly lowered ice adhesion on fishing boat superstructure. Weak electric fields during cure of organosilicone or fluorohydrocarbon increased contact angle and life of hydrophobicity. Increased polyethylene imine and adding

- 83 165898 pigments also increased contact angle. [cf. next]. Fluorocarbon hardened in electric field had only 1.4 psi ice adhesion. As a low energy filler, carbon black can be used in ice repellent coatings. [cf. preceding].
- 84 19402 P Silicone rubber with poly (alkylsilazane), chlorosulfated polyethylene and fumed silica gives low ice adhesion.
- 84 65146 Physical chemical features of base and chemistry of water affect ice adhesion, which is 30% lower for sea water.

Other literature

A considerable volume of articles and reference cards relating to ice adhesion and icing are available in the CRREL library and in personal files of D. Minsk and J. Sayward. Many of course are included among the *Chemical Abstracts* (App. D); some are more recent and/or government reports. Little attempt has been made to cover and digest all of these. An "on-line" machine search by the CRREL Library produced few items of worth.

To approach the questions—What governs ice adhesion? and What chance is there for developing effective low ice adhesion surfaces?—several texts in the field of adhesion, wetting, surfaces and interfacial effects were consulted. These provided foundation for the discussion in *Adhesion and the Interface* above, where they are referenced.

CONCLUSIONS AND RECOMMENDATIONS

1 The chance of obtaining low ice adhesion to combat icing by promoting self-shedding and/or easy ice removal (e.g. by scraping, vibration or shock) in icing situations appears good through attention to the chemistry, physics and geometry of the interface, so as to impair cross-interface exchange of attractive forces and to encourage the occlusion of air at the interface. High droplet velocity and erosion make the helicopter rotor the most requiring case, while air occlusion here may be minimal, improved materials and composites of improved hardness, abrasion resistance, surface flexibility and low surface energy may be useful.

2. Emphasis should be on polymers with hydrocarbon-CH₂- or -CH₃ and fluorocarbon-CF₂- or -CF₃ chains or tails screening other structural components to provide a low energy, inert, hydrophobic, water-repelling, nonwetting, high contact angle surface.

3. To be considered are composites of low energy materials with higher energy materials (organic polymer or inorganic), with either one as matrix or filler, to combine hardness and durability with icephobicity.

4. Besides normal secondary (van der Waals) forces, attraction and adhesion of water and ice to solids is influenced by hydrogen-bonding capability of the substrate. Components capable of hydrogen-bonding (mainly oxygen) should therefore be avoided or well screened in the substrate structure.

5. The attraction of a substrate for ice is directly related to its attraction for water, particularly where hydrogen-bonding is possible. Attraction for water is manifest in determinable properties: contact angle and critical surface tension, which evaluate wettability and adhesion. Determining these should, therefore, guide choice of icephobic surfaces.

6. Occlusion of air at the interface (due to poor wetting, contamination, surface geometry and low energy surface, i.e. preferential "wetting" by air rather than water), appears generally to be a negative factor in all adhesion. By interrupting trans-interface exchange of attractive forces, it lowers adhesion bond strength. By creating irregularities for stress concentration, air patches enhance effects of natural or applied stress in initiating or propagating cracks leading to adhesive failure.

7. Ensuring maximum occlusion of air at the interface should produce minimum adhesion. Means for this include provision of: 1) Low energy substrates, 2) Low energy surface contaminants, 3) Air-saturated water or excess air next the interface, and 4) Optimum geometry of the substrate interface, to maximize θ , minimize wetting, and maximum air occlusion and stress concentration.

8. Construction designs which allow for flexing components during normal use or by provision of an imposed stress intermittently could help initiate and propagate interface cracks and assist ice shedding. Such stress could arise from flexing, shock, vibration or differences in thermal expansion.

9. Survey of the literature, mainly through *Chemical Abstracts*, produced a number of pertinent references. Concepts in some of these may be worth pursuing and prove useful.

10. Contacts with manufacturers turned up some 100 commercial products deemed likely to have low adhesion for ice. Samples of many are at hand and others are sought for testing at CRREL.

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APPENDIX A. Adhesion Testing

In the following, several variations and ideas concerning ice adhesion test methods and factors are briefly discussed. Details of the apparatus and technique used at CRREL will appear elsewhere (D. Minsk, in preparation).

Modes of Test

A. Pure tensile test, where two adhered blocks are pulled apart perpendicularly to the adhesive plane (Fig. A). This may well result in cohesive failure of substrate, since in most cases a well-made adhered joint is stronger than the substrate. With ice on low-adhesion surfaces it might be useful. It does entail essentially instantaneous parting over the whole area, and this may result in high gross failure loads compared to some of the methods below where failure is incremental.

B. Pure lap shear test, where two blocks are pulled apart by tensile stress parallel to the adhesive plane. Actually, depending on the linkage and the rigidity of the components, this may result in some peeling action due to distortion, as shown in Fig. B. The alignment and components distortion problem may be overcome by a sandwich configuration, making stress application symmetrical to a central block with two side blocks and two adhesive planes. With ice as central block it might shatter if pulled but might withstand pushing (see Fig. B). Or layers of ice on either side of a central strong block might work. If rigid and free of distortion, this shear system should also require a large total stress for essentially instantaneous overall failure.

C. Flat plate torsion shear test (90° cone), which overcomes some of the above problems (Fig. C). In one version, the adhesive layer is formed between a fixed plate and a flat disk or annulus, which is then rotated, with measurement of force for failure. Here, intensity of stress or magnitude of strain will vary radially. This may help initiate failure cracks first at (and parallel to (?)) the periphery, resulting in partly incremental, partly instantaneous all-over failure at somewhat lower gross stress.

D. Cylinder torsion shear test (0° cone), where the adhesive layer is formed between a hollow cylinder and central core, one of which is rotated and the torque measured (Fig. D). Here stress should be uniform and symmetrical at all points, failure instantaneous all over, and gross load high.

E. Peel test, adaptable for thin, flexible materials or coatings (Fig. E.). The test strip is adhered (frozen) to a rigid base and an overlapping free end is then pulled away at right angles, measuring the force. The cam device shown could provide for vertical pull. Alternatively, two flexible strips can be adhered and pulled apart. The measured force will be incremental and gross load low; it of course includes what is required to bend the strip. While involving mainly tensile stress, shear may be present, particularly if the strip stretches.

F. Blister test, as cited by Anderson et al. (1974) and ascribed to Williams (1969), (Fig. F). Here pressure is applied at the center of the adhered interface, the upper (thinner, more flexible) member of which is thereby debonded blister-fashion. Forces involved are mainly tensile but could also be shear if the sheet can stretch. The forces are incremental and gross load low; in fact, this permits a series of measurements on one specimen by interruption of the pressure and noting each debond location.

G. Cleavage test (Fig. G). On blocks prepared as for the pure lap shear test, crosswise stresses produce a cleavage starting from one or other edge. Separation forces are essentially tensile (some shear if blocks or adhesive are non-rigid). Failure is ostensibly instantaneous but is actually micro-incremental starting from edge, and the gross load is high.

H. Cone test (Fig. H). Cone angle $0^\circ < \phi < 90^\circ$. Test H_1 - axial force: combination of tensile and shear. Test H_2 - torsion force: shear. In both, failure would be essentially instantaneous and gross load relatively high. (When $\phi = 90^\circ$, \equiv tests A and C; $\phi = 0^\circ$, \equiv tests M and D, for axial and torsion force, respectively.)

A-H are fairly conventional modes of testing. The variations which follow might have some advantage for ice and its adhesion to aircraft.

I. Flexed sheet test, involving the bending or bowing of a flexible sheet coated with a controlled thickness of ice (Fig. I). Force required for ice to separate (including force for bending the test sheet) would be measured. Use of a standard high velocity air flow might assist separation and still more nearly simulate the aircraft situation. If needed, a curved form might control the curvature. Alternatively, the iced sheet (rectilinear or round), held at opposite or all edges, might be deflected by a large-radius section of a cylinder or sphere to assess force to loosen ice. These methods should encourage crack initiation and propagation, giving incremental failure stress and low gross load.

J. Small area tensile test, as between ends of two rods of say 10^{-4} m^2 (1 cm^2) or even 10^{-6} m^2 (1 mm^2) cross-section and tipped with the test material, (Fig. J). This would reduce the chance of defects initiating failure, making specific failure force (instantaneous, all over) higher while requiring less gross force for small area than A.

K. Lap tensile-shear test (Fig. K) where deliberate alignment diagonal to resultant force tends to produce some tensile effect (or peel at edges). Here failure would be instantaneous micro-incremental (like G) or incremental, depending on rigidity of test blocks or coating, requiring large to lower gross load.

L. Multi flat-plate torsion-shear test (Fig. L). A number of individual test blocks ($\sim 5\text{-}20 \text{ cm}^2$ area) might be adhered or frozen in a circle on a large plate and so keyed to a large annulus as to be stressed one at a time successively upon rotation (measured torsion), thus giving a series of replicate tests (like C) with one mounting. Failure should be overall instantaneous or somewhat incremental, and gross load low for small individual areas.

M. Axial cylinder shear test (Fig. M). To a ring and adhered central core (similar to D), apply force axially rather than torsionally to give pure shear (somewhat as in B or D), likewise tending to instantaneous all-over, high load failure.

N. Roll-peel test (Fig. N), a variant of E (less bending of substrate), adaptable for thin flexible materials or coatings. Adhere (freeze) a flexible strip to a heavy plate base, then by a suitable linkage at one end roll the strip onto a large-diameter roll, measuring the force required (would include minor bending). This would be a decidedly incremental separation, essentially tensile and low gross load, perhaps more representative of what happens on flexing aircraft components or overland cables.

O. Combined mode tests. Combined shear and tensile force might prove useful. This could be done by applying a fixed load in one mode while increasing the other till failure. It could be done on most of the preceding. The fixed-variable stress combination should aid in initiation and propagation of cracks to failure and may, then, be nearer field conditions, notably for aircraft.

Other Comments

Adhesives commonly shrink upon drying or setting. For ice, however, solidification is accompanied by expansion. This could affect some of

the above test schemes where a film of ice is to be formed in a confined space. Because ice is both brittle and not strong in either tensile or compressive mode, the stress developed on freezing might cause cracking, producing a cohesive breaking before adhesive failure. Or, its expansion on freezing might damage apparatus in some cases if frozen rapidly and homogeneously.

As has been indicated, different results may be anticipated using different methods. This is seen in report of the mechanics and energy balance of debonding polyurethane adhered to polymethylmethacrylate by Anderson et al. (1974). The scanning electron microscope (SEM) was used to study the adhered surfaces after debonding by three different modes. Both fracture energy and residual roughness were found to increase in the order:

Loading mode I: normal separation, mainly tensile - crack surfaces move directly apart; most like modes A, E, F, I, J, N.

Loading Mode II: cylinder shear, sliding shear - crack surfaces overslide \perp to crack; most like modes B, D, M.

Loading mode III: flat plate torsion shear - crack surfaces overslide \parallel to crack; most like modes C and L.

In absence of actual trials and examination of crack habits, it is expected that the several test modes described above and shown in Figures A-L would fall into the loading modes cited by Anderson et al. (1974) as follows:

<u>Test mode</u>	<u>Loading mode</u>	<u>Failure^a</u>	<u>Gross^b load</u>
A Pure Tensile	I tensile	0	h
B Pure Shear	II \perp overslide	0	h
C Flat Plate Torsion Shear	III \parallel overslide	i-0	h-l
D Cylinder Torsion Shear	II	0	h
F Peel	I	i	l
F Blister	I (II if stretch)	i	l
G Cleavage	I	0	h
H ₁ Cone Tensile-Shear	I & II	0	h
H ₂ Cone Torsion-Shear	II & III	0	h
I Flexed Sheet	I	i	l
J Small Area Tensile	I	0	l*
K Tensile-Shear	I & II	i-0	l-h
L Multi- Flat Plate Torsion-Shear	III (or II)	0-i	l

M Axial Cylinder Shear	II	0	h
N Roll-Peel	I	i	l

a) Failure: 0 = overall-instantaneous; i = incremental

b) Gross failure load: h = high; l = low

* High specific load.

The proposed CRREL tests are in mode C, i.e. loading mode III. They may be expected to give higher test results for ice adhesion strength than would some others, because of the overall instantaneous failure.

Loosening of ice from an aircraft member or a cable may less likely involve shear and more likely propagation from local loci of stress or cracks and springing free (tensile mode) by flexing and/or action of high velocity air flow and/or centrifugal force. Perhaps, then, the Type I (tensile) tests should be considered, e.g. modes A, E, F, G, H₁, I, J or N as described above.

Another factor in adhesion tests is air at the interface, as discussed previously. It was suggested that the use of "de-aired" water might give higher values and more variability (due to inability to maintain water 100% air free during handling) than would use of air-saturated water. Though the former was initially planned for CRREL tests, the latter may be preferable - nearer field conditions and more consistent (and likely giving lower adhesion). The two should at least be compared.

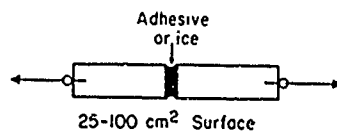


Figure A. Pure tensile test.

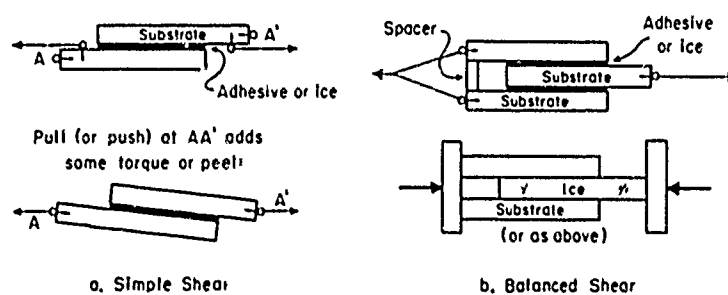


Figure B. Pure shear test.

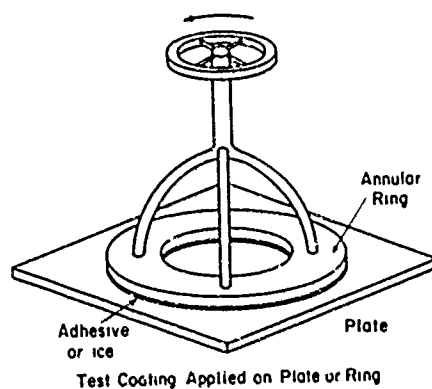
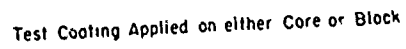


Figure C. Flat plate torsion shear test (CRREL mode).



Wheel with cam to keep peel pull vertical (cf. AA' vs. BB')

Flexible Strip

Rigid Base

Adhesive or Ice

Test Coating Applied on either Base or Strip

BB'

AA'

Cord

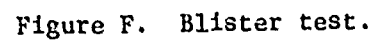
Flexible Strip

No rigid base needed

Test Surface on one or both Flexible Strips

b. Split-mode.

Figure E. Peel test.



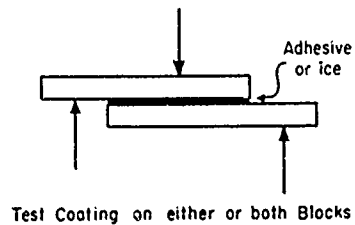


Figure G. Cleavage test.

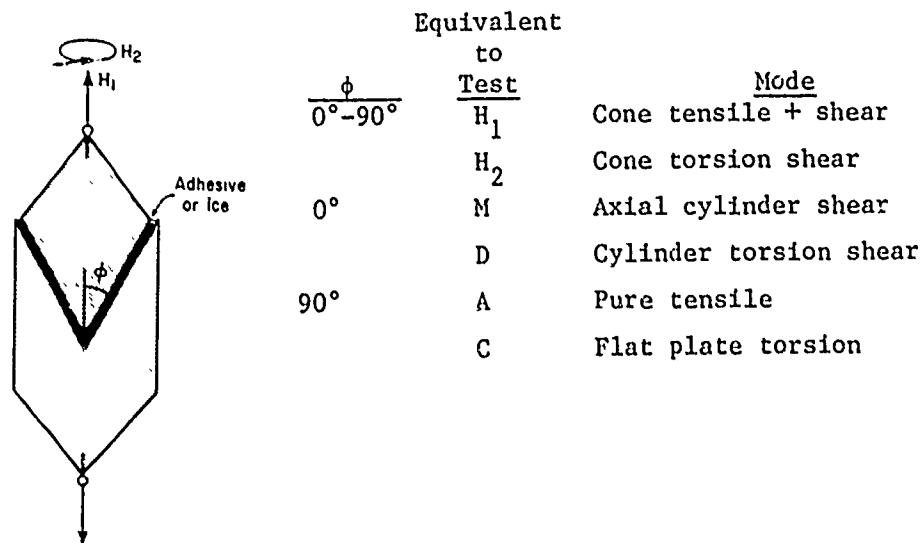


Figure H. Cone tensile-shear test.

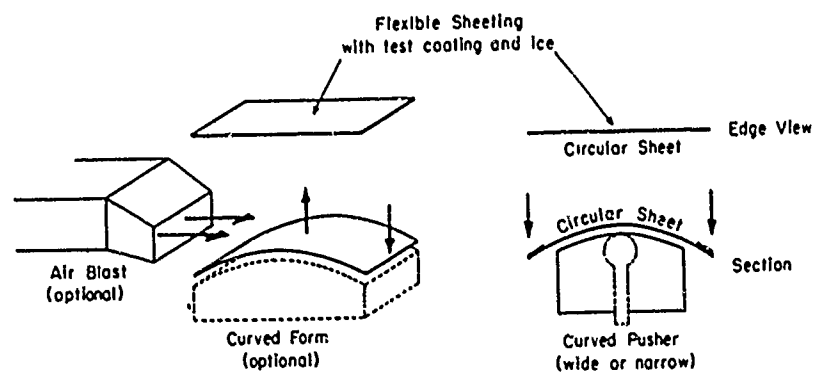


Figure I. Flexed sheet test.

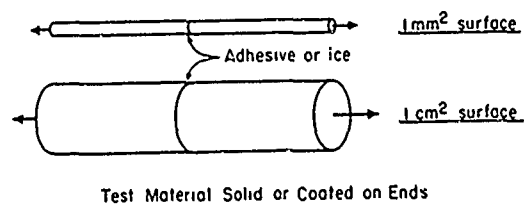


Figure J. Small area tensile shear test (cf. Test A).

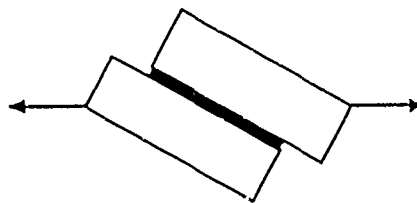


Figure K. Lap tensile-shear test (cf. Test B).

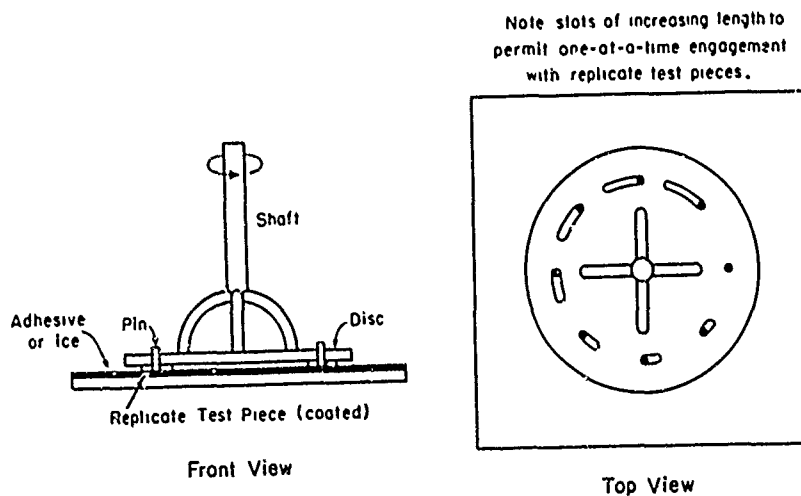


Figure L. Multi flat-plate torsion shear test (cf Test C).

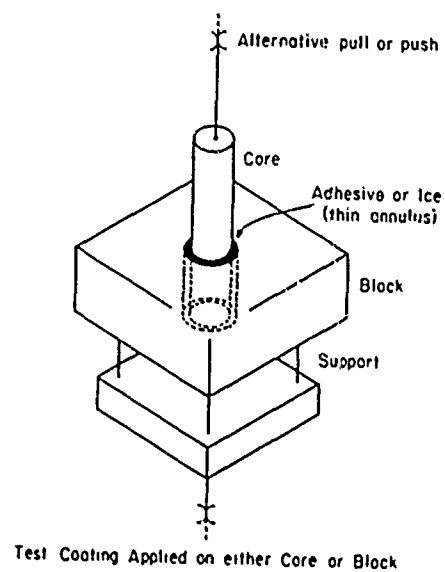


Figure M. Axial Cylinder Shear Test

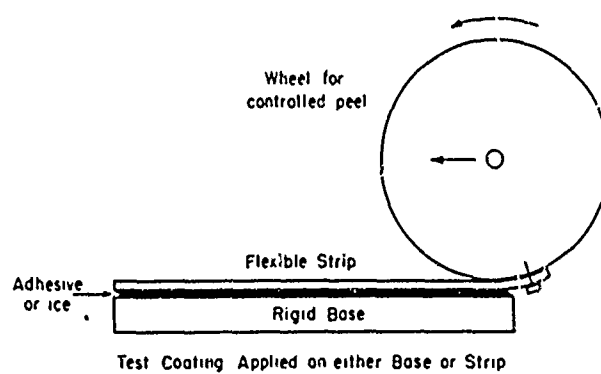


Figure N. Roll-Peel Test

APPENDIX B. Listing of Commercial Products

Industrial Products

Here follows an alphabetical company by company listing, with brief narrative descriptions of products which from the information furnished are so far judged of sufficient interest to request samples for current testing of ice adhesion at CRREL. Samples of some are already at hand, expected of most others. Company addresses are in Appendix C. Codes at left indicate rating judged on information available (recommended order of testing: group A (best) to group C, rated 1 - 3 within groups).

Allied Chemical Corp.

(A-1) CM-1 Fluor Copolymer, a highly crystalline copolymer of hexafluoroisobutylene and vinylidene fluoride--generally superior to other fluorocarbons in hardness, abrasion, heat, chemical and water resistance and impermeability; adheres to metals. Application: melt processable (can be fusion coated from powder).

American Technical Industries

(A-2) ATI-KOTE 550, aliphatic polyurethane coating (two component), a polyester blend and aliphatic isocyanate--smooth, hard, resistant to moisture, chemicals, solvents, abrasion; long life, adheres to metals, masonry, wood (usually needs no primer). Application: mix the two parts 15 minutes before use; use brush, roller, or spray; pot life 6-8 hours. ATI reports simple ice adhesion test: coated steel plate frozen into ice in bucket, bucket dropped a mere 6 in., test plate slid out ice-free from unbroken ice, whereas uncoated steel plate remained frozen in until drop was increased to 24 to 36 in., breaking ice but leaving 1/8 in. ice on steel.

(B-3) ATI-KOTE 511, urethane coating, single component reactive prepolymer--smooth; hard; resistant to water, chemicals, and solvents; rust undercutting. Application: use brush, roller, or spray. Can be used as primer for #550.

Armstrong Products Co.

(C-1) Vibro-Flo PE 5000, thin-film, thermosetting polyester coatings--smooth, tough, durable, flexible, resistant to abrasion, weather and chemicals; long life. Application: melt processable (fusion coated powder). Also have E-7000 similar epoxy type powder coatings.

(C-2) Special-T Resin T-230, epoxy (two part) - very hard, abrasion resistant, durable, wear resistant. Application: mix 7:1 by volume (spray or brush), pot life 1/2 hr., cure 16 hours at RT (room temperature).

(C-2) A-2/W and C-7/W, epoxy adhesives--low thermal expansion, flexible. Application: brush; pot life 1.5-2 hrs.

Axel Plastics Research Laboratories, Inc.

(B-2) Mold Wiz, non-silicone, non-wax, non-stearate mold releases--good adherence and durability: AZN, solvent solution, #249, emulsion, F-57, buffered fluorocarbon solution. (Likely impermanent.)

Cabot Corp.

Finely divided fumed silica (made by pyrolysis of organic silicone compounds). In hydrophobed, e.g. silaned, form, this is of interest as an additive to convey water repellency to resins and coatings. The hydrophobed part of Cabot's fumed silica business is handled by Tulco, Inc. (see below).

Caig Laboratories, Inc.

(B-2) Cramolin Spray R, a mineral oil, non-acid anti-oxidizing lubricant and cleaner--"lasts for years." Intended for electrical contacts; they believe will repel ice. Application: spray (Freon aerosol available).

(B-2) Cramolin Carbo Spray, contains graphite for similar purposes--may give better results than Spray R.

(B-2) Cramolin Plastic Spray, acrylic--seals, protects, water repellent, chemical and weather-resistant. Application: spray (Freon aerosol).

(All likely impermanent.)

Carboline Co.

- (C-2) Modified epoxy
(B-1) Tough elastomer

} Under development, details not given.

(B-2) TOXSTOP, non-silicone water repellent barrier for waterproofing and sealing concrete, stone and masonry--allows interior moisture to escape, resistant to weathering (UV), abrasion, and water. Application: clean dry surface, use spray; dry in one hour. Three grades available: Limestone Sealer 633, Regular Sealer 635 (for concrete, etc.), and Heavy Duty Sealer 640 (for more porous surfaces).

The Carborundum Co., Dielectrix Div.

(A-2) Teflon-Al₂O₃ composite--recently developed to give improved abrasion resistance while retaining fluorocarbon hydrophobic property. Development suspended in favor of following (better to abrasion?).

(A-1) Teflon (PTFE)/Kapton (polyimide) micro-multilaminar composite--very thin layers completely fused (free of usual microporosity of PTFE). Has FEP backing for heat sealing to metal. Kapton core gives strength and abrasion resistance, Teflon hydrophobicity, impermeability and tear resistance; Teflon/Kapton ratio can be varied for optimum performance. Believed superior to Teflon-Al₂O₃ composited (above), work on which is suspended, but the two could be combined. With FEP backing, can be heat sealed.

(A-1) DF-3200--an ultra-high molecular weight polyolefin hydrocarbon tape with arylic adhesive backing. Has very low coefficient of friction, highest impact strength of any thermoplastic, wear resistance like steel or better, exceptional abrasion resistance. Can have acrylic pressure-sensitive backing.

The Ceilcote Co.

Epoxy lining--very smooth, hard surface, once supplied for trial on concrete locks in Canada to control ice build-up. It was a one-shot try, and they don't know results; the product has since been discontinued.

They suggested that the Garlock Co. (mfrs. of gaskets and packing) makes a Teflon-filled coating of possible interest.

Celanese Plastics Co.

(A-1) Celgard microporous polypropylene (PP) film, inert, hydrophobic, permeable to gases and liquids of low surface tension and

viscosity; porosity ca. 40%, pore size 0.02 or 0.04 μ m; can be metallized, or laminated, e.g. to non-woven PP fabric. (Might be impregnated with icephobic liquid for anti-ice use.)

Contour Chemical Co.

(B-3) Variety of release agents (mainly aerosol sprays), some described as non-silicone, others unspecified. (Likely impermanent.)

Cook Paint & Varnish Co.

(C-1) Acrothane White 975-W-4267, an acrylic urethane enamel, two-part--high gloss, hard, durable outdoors, tough, resistant to abrasion, solvents, chemicals. Application: (on metal after copoxy or zinc chromate primer), mix 4:1 five minutes before use, spray; pot life 6 hours; cure overnight at RT.

(B-2) Silicone-Acrylic Gray 881-A-001, two-part--glossy, hard, durable outdoors. Application: sandblast steel (no primer needed), mix 16:1 by volume very accurately with curing agent 700-C-418 15 minutes before use, spray; pot life 4 hours; cure for 24 hours at RT (needs no curing agent if baked).

Custom Compounding

(A-3) Polylube J, a PTFE (polytetrafluoroethylene)--very hydrophobic (surface tension only 17 dynes/cm²), very low friction (static friction coefficient only 0.02), resistant to water, chemicals and weather; can be incorporated into matrix of elastomers, metals and plastics for long wear and low friction. Application: spray (available in CO₂ aerosol can). (Likely impermanent.)

de Beers Laboratories, Inc.

(A-2) Debron 711, non-stick PPS (polyphenylene sulfide, a material found best of six tried, including Teflon, in ice release studies by the Navy Aeromaterials Lab (Williams 1973), water based--durable, non-stick, low friction.

(B-2) Debron 713, PPS, water based--extreme chemical resistance, same as 711 except not non-stick.

(A-3) Debron 611, non-stick silicone.

(B-2) Non-stick polyimide polyimides tend to be strong, tough, durable, low-friction and to resist chemicals and wear--release and low friction at high heat, non-stick.

Dow Corning Corp.

(B-1) 330 Fluid, a methyl silicone fluid--water and ice repellent, intended uses include electrical, thermal, hydraulic, lubricant and ice release; used on commercial and private aircraft to prevent ice build-up. Application: brush (or wipe). (Likely impermanent.)

(B-1) 5-Compound, a silicone grease--water and ice repellent, inert. Extensively studied by NOAA (Nat. Ocean. & Atm. Adm.) and found successful for protecting ship antennae insulators from salt-water-induced leakage. Application: brush (or wipe). (Likely impermanent.)

(A-2) R-4-3117 Conformal Coating, a transparent silicone resin--flexible, moisture and weather resistant, used for coating circuit boards and sealing porous substrates. Application: clean (no primer needed), spray, dip, brush or flow coat; cure in 24 hours at RT, or, by using 1/2% XY-176 catalyst, in 1/2 hour at 168°F (75°C).

(A-3) 3-5000 Construction Coating (Silicone Rubber Coating)--resistant to weather, ozone, UV, chemicals; durable, waterproof (yet breathes water vapor). Used to coat urethane insulation on roofs, ducts, etc. Application: sand blast and apply primer; use brush, roller or spray; dry in 2-6 hours; cured in 3-7 days.

(B-1) ARC (Abrasion Resistant Coating), silicone resin--extremely hard, clear, adherent; abrasion, weather, moisture, solvent and chemical resistant. Application: dip, spin-flow or spray, in clean room; oven cure. Main use is for protecting softer transparent plastics (eyeglasses, windows, instrument glasses, etc.)

E.I. duPont deNemours & Co. (see also Boyd below)

(A-1) Teflon-P PFA Powder Coating 532-5010, perfluoroalkoxy polyfluorocarbon--thermoplastic, non-stick, non-wetting, low friction, good adhesion, resistant to weather and chemicals. Application: grit blast, use primer for best adhesion, apply as powder by electrostatic spray, fluidized bed, etc., followed by fusion.

(A-3) Teflon, PTFE Coating 851-204, polytetrafluorethylene, for use as primer or one-coat -- very high release, low friction and non-stick; excellent adhesion to most metals (not to >0.5% magnesium alloys), glass, porcelain, etc.; water, abrasion and corrosion resistant. Application: sandblast, agitate container (water dispersed) spray (use acid-resisting equipment), dry at 218°F (82°C), bake: as primer, 3-30 minutes at 450-550°F (232-288°C), as one-coat, 5-10 minutes at 725-775°F (385-413°C).

(A-2) Teflon FEP Finish, 856 Line, fluorinated ethylene propylene copolymer--melt-flowable, non-porous, high release, low friction, excellent abrasion, chemical and corrosion resistance. Application: grit blast, use primer, agitate (roll) container (liquid dispersed), then filter (100 mesh), preheat substrate to 120-140°F (49-60°C), spray (regular or electrostatic), bake 60-5 minutes at 575-700°F (302-371°C).

(B-1) VYDAX 550, fluorotelomer dispersion (5 µm particles)--white, waxy, short chain telomer of PTFE in Freon TF (trichloro-trifluoroethane) solvent. Low friction, release, stable. Adhesion improved by added binder (consult aerosol mfrs.) or by fusion at 570-600°F (300-316°C). Used for lubricant, release, paint additive to improve wear. Application: clean, dry surface; dip, wipe, spray, electrostatic. (Likely impermanent.)

--Boyd Coatings Research (licensed applicator for duPont)

(A-1) Fluorocarbons and Combinations, a variety of powder-fusion coatings based on duPont's Teflon PFA, FEP and PTFE, Pennwalt's Kynar, Allied Chemical's Halar (all fluorocarbons), and PPS (polyphenylene sulfide, Phillips Chemical), polyimide, silicone and polyurethane resins. Most of these are composites or "plastic alloys" and are harder but have the release, low friction and hydrophobic properties of fluorocarbons.

--Other nearby duPont applicators contacted, offering variety of Teflons and composites:

--American Durafilm Co., Inc.

--The Donwell Co. (will prepare any Teflon on our panels).

--Precision Products Co.

--Duralectra (parent of Precision Products, active in anodizing aluminum; offers "Hard Lube").

Durok Building Materials, Inc.

(B-1) Durok Duroplex II, nature unspecified, two-part masonry (concrete) protection against dirt, water penetration and spalling--invisible, allows "breathing," anchors in surface pores, resistant to moisture and freeze/thaw. Application: mix two components 9:1, use spray, brush or roller.

(B-2) Durok Shield, a polyvinyl-acrylic compound modified with chlorinated triphenyl for maximum water-retention and salt-resistance, for masonry--anchors to surface, seals out deicer solutions to prevent spalling; dustproofs, hardens and seals surface, indoors or out; durable even under heavy traffic. Application: on good new concrete, when firm enough to walk on, spray two coats or roll one coat; on old concrete, roll, brush or spray two coats.

(Possibly of interest for canal locks, etc.)

Easton R.S. Corp.

(B-3) Wax Emulsion StSt, mixture of hard and soft waxes emulsified in water (no solvents), with small % of high molecular weight silicone oil coupled with a phosphate ester--usable at high pH (as shipped), neutral or low pH; high gloss, release agent, corrosion preventive. (likely impermanent.)

Elastomer Sales Co.

(B-3) Port Poly HDPE Film, high density polyethylene film (extruded by Port Poly Co.) mfd. by Hoechst or Union Carbide, comes up to 60 in. width; more durable than normal PE. (Possibly of interest, with stiff backing, for canal locks).

Essex Chemical Corp.

(B-1) Betacote 91 Series Urethane Coatings, high gloss, inert, flexible; abrasion moisture, solvent and chemical resistant. Application: clean (preferably sandblast), use primer; mix 3 to 15 minutes before use, brush or spray 2-3 coats; pot life 6-8 hr; cure 4-24 hr between coats (for brushing, thin first coat 30%, others 10% with Betacote 91-100; for spraying thin up to 15%.

(C-3) Betacote 75-14, zinc chromate wash primer, for non-porous metals. Application: clean (sandblast preferably), mix A:B 3:1, brush or spray one coat (thin up to 20-30% with Betacote 80-100); pot life 6-8 hr; cure 1/2-8 hr before finish coat; clean-up: Betacote 80-100 or alcohol.

General Electric Co. (Central Research & Plastics Depts.)

(A-1) Silicone-polycarbonate (PC) block copolymers in which silicone components predominant in the surface are believed to give low ice adhesion. Of many research products, 5530, 3320 and 4330 have been produced commercially. The 5530 is similar to LR 5630, used with 10% free silicone oil present in a promising canal lock anti-ice coating (Jellinek 1974-78). The powdered resins are applied as roughly 10%

solutions in toluene, in which the free silicone oil is added for the lock coating. This soft, pliable coating was tried at three locks in winter 1977-78, with encouraging results.*

General Electric Co. (Silicones Dept.)

(B-1) New hard silicone (siloxane) polymers, solvent-applied (best to use primer), require 30-40 min. cure at 120°C (248°F), abrasion-resistant (intended for protection of other plastics, as in windows). Have also grease-like silicone materials, e.g. C-697 silicone oil with silica filler, being tested at Army Mobility R&D Lab.

General Magnaplate Corp.

(A-1) Lectrofluor 405, now called Tufram PG-405, a new material they have developed to resist ice formation, recently proved out in tests by the Boeing Co. Details of composition, properties and application not yet furnished.

Goodyear Tire & Rubber Co.

Polyurethane-Polycarbinol Silicone Copolymer, specially developed (BP 1,477,055), cited in New Scientist 18 Aug. 1977, p. 415, as preventing icing. Composition, properties and application not given. Was submitted for Coast Guard ice breaker tests for low friction, reported in 1974, and for Army helicopter anti-icing in November 1974. In the former, Goodyear writes, it was not successful - became detached - and material is not available now.

Groendyk Manufacturing Co.

(A-3)	<u>8604 Solid Silicone Sheet</u>	} Silicone rubber molded sheets, varying flex-ible.
	<u>8804 " " "</u>	
	<u>8203 " " "</u>	
	<u>7504 Silicone Sponge Sheet</u>	

*B. Hanamoto, CRREL, personal communication, 1978.

Hauser Laboratories

A development, testing and design laboratory specializing in polymeric and composite materials. They cite two projects of interest.

Have tested shear strength of ice bonds to surfaces, particularly on Ball Brothers Research Corp. project for EPA for treatment of highways to reduce ice adhesion (Ahlborn and Poehlmann 1976).

Helped develop a chrome/Teflon system for TFB, Inc., whose "Kro-Lon Surface" brochure they sent. See TFB, Inc., below.

The O. Hommel Co.

(A-2) R 1185 (aluminum enamel 05556-C), alkali lead silicotitanate procelain enamel frit--intended for aluminum appliances and sanitary ware, melts ca. 1000°F (540°C); smooth, hard, durable, resistant to water, chemicals and weather; (coef. of expansion not given). Application: spray, dip or powder fusion methods. A similar frit for iron (#5588) is also an alkali lead silicotitanate, has coef. of expansion $13.9 \times 10^{-6}/^{\circ}\text{C}$, melts around 1000-1150°F (538-620°C) and requires a base coat (#5803, an alkali borosilicate).

Hughson Chemicals - Lord Corp.

(C-1) #9922 Epoxy Metal Primer, two-part epoxy resin--adherent to steel (sandblast); resistant to water, salt water and corrosion. Application: mix A:B 3.5/1 by volume, use spray or brush; pot life ca. 8 hours; cure 2-20 hours.

(C-1) #9924 Wash Primer, two-part, modified polyvinyl butyral resin and phosphoric acid catalyst--adherent to aluminum and other non-ferrous substrates, highly flexible, resistant to impact, water, salt water and corrosion. Application: mix A:B 1:1 by volume, use spray; pot life 8 hours; cure: dry to tough in 1 hour.

(C-1) Chemglaze Elastomeric Polyurethane Coating, two-part, tough, flexible, wear-resistant, not UV resistant (to use as intermediate coat between primer (above) and topcoat (below). Application: mix 2:1 to curing agent M200 (which is moisture sensitive), use spray; pot life 1/2-2 hours.

(B-1) Chemglaze A (Chemglaze II), polyurethane (pure, no extender), one-part--excellent gloss retention; resistant to abrasion, impact, weathering, chemicals and solvents. Application: on one of above primers and intermediate coat, apply by spray, dip or flow-coat (not roller); cure: dry in 2 hours, hard in 6-12 hours, full properties in 10-14 days (if catalyzed, dry in 1 hour, hard in 4-8 at RT); if baked at 250°F (121°C), hard in 15 minutes (5 minutes if catalyzed).

Impact Plastics, Inc.

(A-2) Impax, an ultra high molecular weight polymer (nature unspecified, probably polyethylene, UHMW PE, described in Modern Plastics Encyclopedia), low friction, self-lubricating, durable, high impact, abrasion and chemical resistance. In various wear applications, will outwear even exotic metals, nylon, urethanes and fluoroplastics. Available in sheets up to 4x10 ft.

MAMECO International (The Master Mechanics Co.)

(B-2) Vulkem Sealants and Membranes, one part modified polyurethane rubber, resistant to aging, weather, moisture, solvents, chemicals; flexible; adherent to concrete, ceramics, steel, wood. Intended for walls, decks, tanks, etc.; can protect concrete from freeze/thaw. Application: apply liquid direct (no primer) by spray, squeegee, roller, brush or trowel; cure two days (by atmospheric moisture) or can be catalyzed; can be applied at sub-freezing temperatures. (Might serve for anti-icing on canal locks?)

M&H Laboratories, Inc.

(B-1) #1604 Ice Repellent, silicone--affinity for metal substrates, repels ice from snow-handling equipment and metal linkages on vehicles, etc. Application: by spray (airless best). (Likely impermanent.)

Miller-Stephanson Chemical Co.

(B-2) MS-122 Fluorocarbon Release Agent Dry Lubricant. Application: dip, spray, brush or wipe.

(B-1) MS-136, same as MS-122, but in less volatile solvent.

(B-1) MS-143 Fluorocarbon Mold Release and Dry Lubricant, in fluorocarbon solvent system. Application: brush or spray.

(A-3) Teflon Telemers, with polar end groups to improve bonding to substrate. (Source of this uncertain, but they offered they might get an aerosol can for test).

(All likely impermanent.)

Olin Corporation

Manufactures raw materials not coatings, but in 1967 Olin Research Center developed a rain erosion-resistant urethane coating, ASTROCOAT (MIL-C-83231), now used on many aircraft. It is produced by Sterling Manufacturing Co., see below.

C.J. Osborn Chemicals, Inc.

(B-1) Silicone Resin Finishes, high silicone content--high resistance to weather, water and chemicals.

(B-1) Fluorinated Compound Resin--anti-stick, wear-resistant. Details on properties and application not yet at hand.

Peterson Chemical Corp.

(A-1) Teflon Epoxy Coating #4, a two-part epoxy with Teflon particles dispersed--low friction, excellent slip and release, strong adhesion to substrates (wood, metals, fiberglass, concrete, many plastics, ceramics, porcelain, tile, bricks, etc.); tough, durable, flexible, very low water transmission. Application: stir each, mix A:B 1:1, apply by brush, roller, or spray, two or more coats; pot life up to 3 days; final cure 7 days at RT, or 40 minutes at 150°F (66°C). After cure, wet sand with #600 grit paper or buff well with fine steel wool to expose embedded Teflon.

(C-2) Zinc Chromate Epoxy Primer #6, two-part (no product information yet furnished; probably to be used under #4).

Phillips Chemical Co.

(A-2) Ryton, polyphenylene sulfide (PPS) resin--release, non-stick, hydrophobic (contact angle similar to that of Teflon); highly inert, hard; resistant to heat, corrosion and wear; has affinity for fillers, including PTFE and graphite; can apply by slurry, electrostatic or other powder methods, but requires high temperature fusion cure (20 min. per mil at 380°C (700°F)). PPS was found best of six candidates tried in ice release tests by the Navy (Williams 1973).

REN Plastics, a Ciba-Geigy Co.

(A-2) REN-FLEX Thermoplastic Elastomer, modified polyolefins, an inter-penetrating matrix system bridging crystalline and amorphous phases--can be molded and thermoformed; low-temperature impact toughness, flexible, high abrasion and tear resistance, resistant to scratch and mar and to environment (excellent resistance to UV); can be painted or filled with carbon black. Application: formed as molded or extruded sheets--would have to be attached, adhered, fused or integrally molded (laminated) onto substrate; (since thermoplastic, conceivably could be made as fine powder and powder-fused (?)).

Rilsan Corp.

(A-3) Rilsan Nylon 11, a polyamide derived from vegetable, not from petroleum materials (as are other nylons)--thermoplastic, low water absorption (in contrast to other nylons), dimensionally stable, low friction, resistant to environmental, oxidation, abrasion, impact, chemical, and corrosion effects; has elastic memory, sp. gr. only 1.04; can produce fused coatings; can have filler of glass for strength or graphite or MoS₂ for lower friction and better wear. Application: fusion coating (fluidized bed or electrostatic).

Skinner & Sherman, Inc.

This testing lab says they have done in-house product development in the anti-icing (Teflon-based) area for clients but cannot release proprietary information. They do testing, not research, and are anxious to cooperate in testing. To our inquiry, they report client has no interest in our project at this time (client's identity unrevealed, so we can't approach him.)

Specialty Products Co.

(B-2) Kant Stik LM, a mixture of fatty acid condensed and esterified organic acid in long molecular chains, in aqueous solution or dispersion, capable of forming a water-resistant film, a dry-film mold release (lasts 20-50 shots). They believe it would serve in anti-icing with desired permancece, erosion resistance and adherence. Application: clean surface, spray, brush or wipe. (Likely impermanent.)

Springborn Laboratories, Inc.

(A-1) Porous Plastics, can be oil-impregnated. Springborn has U.S. and Canadian patents on technology for making various plastics porous, e.g. 40-70% voids, 0.05-2.5 mm thick sheets, 0.1-0.9 mm interconnecting pores. A variety of suggested uses include impregnation with silicone or fluorocarbon oil. Exudation of such oil should reduce ice adhesion, as well as friction. As Springborn is important in research, not production, off-the-shelf products are not available (and no client has as yet taken up production of such products). However, their simple trial of fluorocarbon oil-impregnated polyethylene with ice was encouraging. They propose doing Army-sponsored research on our problem and in turn would grant the U.S. government a free license in the limited area of helicopter blade use.

NOTE: The above scheme resembles the idea proposed some years ago at CRREL (Plump and Engelberth 1964, Plump 1968), of impregnating ("dissolving" in this case) an oil, such as pristane, into polyethylene, to exude as temperature fell and solubility decreased, thereby greatly reducing the strength of ice adhesion.

StanChem, Inc.

(A-2) 85X-162 Clear Silicone Finish, one-part--smooth, weather and stain resistant, low friction. Application: dilute, apply by spray or dip to clean metal (primer optional), cure 30 minutes at 250°F (121°C).

(B-3) 66X-3157A Wash Primer, a two-component polyvinyl butyral-zinc chromate. Application: mix 1:2 with 80X-342 activator thinner, spray; pot life 8 hours; cure: air dry 10 minutes at RT before top coat.

(B-1) 67X-1028 White Silicone Enamel--high heat and weather resistance. Application: dilute, spray on metal, cure 1 hour at 400°F (204°C) or 1/2 hour at 425°F (217°C).

Sterling Lacquer Manufacturing Co.

(A-1) ASTROCOAT, urethane coating, developed in 1967 by Olin Corp. Research Center to resist rain erosion, MIL-C-83231, now replacing neoprene in 95% of military, 50% of commercial aircraft. Olin has no anti-ice information but believes such available somewhere. Says it has been used at 20+ mils on Sikorski's fiberglass rotor blades, especially on the outer 6 ft, for seven years, to protect from rain and sand erosion. Also used in other aircraft applications, e.g. by Air Force on radomes, antennas, leading edges. Boeing (at Menton, Wash.) might have anti-icing performance as to use on radome discs on B-727's modified for AWAC. (Info from Olin.)

Stoner's Ink & Chemical Co.

(B-2) C541 Silicone Spray, a high viscosity silicone oil--release agent, stands high temperatures.

(B-2) A885 Silicone Spray, dimethyl silicone oil (10,000 centistokes viscosity) in hydrocarbon solvent, 4% solids--high film strength, all purpose release.

(C-3) B223 Silicone Resin Rust Preventive.

(B-3) Mold Release D430, silicone catalyzed mold release, in solvent, semi-permanent, stands high temperature. Application: spray; cure: 550-600°F (288-316°C).

(B-3) Fluorocarbon Mold Release Dry Lubricant, spray--release, anti-stick, for machines and sliding components.

(B-3) Cl46 (for cold), B660 (for hot) Fluorocarbons, spray--dry lubricant, anti-stick, release.

(B-3) Friction-Free Silicone Spray--low friction, anti-stick, lubricant, waterproofer, used on snow shovels, and to repel ice from locks and auto lids.

(All likely impermanent.)

SWS Silicones Co. (owned by Stauffer Chemical and Wokker Chemie of Germany)

(A-1) Silgan, a silicone graft polymer composite including accicular reinforcement (rods of styrene or acrylic resin). It is much harder and stronger (higher modulus) than conventional silicones while retaining their low surface tension. They cure by ambient humidity or catalyst at ordinary temperatures and are easily applied to many materials, including more flexible substrates, e.g. foamed elastomers. (It thus might be of use for the Sewell flexible substrate system.) They tried it with silaned sand five years ago on company walks to repel ice. This it seemed to some extent to do and is still in use, though no development has been undertaken. Specific products are:

(A-1) Silgan Elastomers H-621 and H-622, two-component (catalysed). H-622 is less viscous liquid but when cured is stronger and harder and tougher.

(A-1) Silgan Elastomers J-500 and J-501, paste and dispersion, respectively, one component, poorer strength, more flexibility.

- RTV Adhesive Sealant 951, one component, for bonding silicone rubbers to metal and glass.

- SWS 409, 415, and 417 Primers, RTV silicone rubbers to improve adhesion of the above to sythetic resin, porous (masonry and rock) and non-porous (metal and glass) materials, respectively.

TFB, Inc.

(A-1) Kro-Lon Surface, a chrome/Teflon composite tooling surface formed by producing a chrome plating with micropores (<10 μ m) which are then thermo-mechanically loaded with Teflon (surface 60% chrome, 40% Teflon)--hard, abrasion resistant, low friction, lubricant, durable. Intended for heavy duty tools, as for pipe bending. Application: would have to be factory-produced onto metal parts supplied, or produced on metal sheets attachable in shop or field. Present plating tanks limited to 24-x-48 in.

Tulco, Inc.

(A-3) Tullanox 500, fumed amorphous silica powder hydrophobed with organic silicone-like compound, highly water repellent, (can "emulsify" water in air to make it behave like a dry powder), very fine, light, fluffy, dusty particles that are non-porous but of high external surface area per gram; when added to other coatings, makes them hydrophobic.

(A-1) Tullanox LC410, concentrate of Tullanox 500 in solution of acrylic copolymer in a liquid hydrocarbon--for formulating highly water repellent coating systems without problems and hazards of handling the dusty material. Said to produce hydrophobic micro-roughness on surface of coating, which then holds water droplets away and traps air beneath in the roughness, much as seen in nature when insects and foliage trap air on a waxy, micro-fiber-coated surface, producing a silvery sheen or "gaseous plastron (shield)" effect. (This seems particularly intriguing, even if not adaptable to high speed droplet impact on aircraft.)

(A-1) Tulcote 22, a suspension of Tullanox 500 in polyhydric alcohols, water dilutable--for hydrophobing masonry, wood, etc., by impregnation into pores.

C.W. Estes Co. (formulator for Tulco, Inc.)

(A-1) Vellox 140 (Hydrophobic Yacht Coating), Tullanox in special resin formulation - produces "gaseous plastron" of air between hull and water reducing turbulence and drag (used on two America's Cup racers). Also suggested for electrical and waterproofing purposes. (May not resist abrasion.)

(A-3) Astro Sand (Hydrophobic Sand), 70-100 mesh, might be applied to paint in tacky stage to produce non-slip icephobic surface.

Have had some materials out for test on pavements this winter, with success. Working with some 20 different applications of Tullanox.

Silobond Products Co. (formulator for Tulco, Inc.)

(A-1) M77-030 Product, newly developed coating incorporating Tullanox in acrylic or silicone resin with solvent - adheres to metal, wood, masonry, fabric. Available for spray or brush application.

(A-2) Hydrophobic Tile, compressed hydrophobed sand (weaker than concrete) hydrophobic throughout structure.

(A-3) Hydrophobic Sand, 30-80 mesh, has been found effective as ice anti-skid on steps.

Tullanox is being put into hydrophobic coatings for windows, metal, masonry, wood, clothing.

UNELKO Corporation

(A-3) REPCON Rain Repellent and Surface Conditioner, activated isomeric polymers catalyzed by isopropyl hydrogen sulfate, one of a line of transparent polymer coatings making glass, transparent plastics, etc., highly water repellent (patented), used on aircraft windshields, etc., for rain, snow and icing conditions, e.g. by the Air Force on nearly all its aircraft; meets MIL-W-6882 (AS), stock listed under NSN 6850-00-139-529. Adherent to substrate as thin monomolecular film (won't stick to itself and thus can't build up), water repellent, reduces friction, abrasion and weather and chemicals resistant, reduces electrostatic and foreign matter adhesion. Application: by wiping (no surface preparation needed). (Likely impermanent.)

Union Carbide Corporation

Report several interesting ideas generated when our survey letter circulated among their Silicone and Plastics group, and test samples could be provided. No details given, but we have requested what info and samples they can send.

Vita Corporation

(B-2) MES-5 (white cover), non-wax moisture repellent with binder, specially formulated for us. Application: spray.

(C-1) MES-5 (brown cover), standard rust preventive, has non-drying resin--remains tacky and flexible, will kill rust and combat salt corrosion, intended for auto underbodies, but tacky feature may repel ice. Application: spray.

(Both likely impermanent.)

Vitek Research

(A-2) (Several unique products). Have patented process for pore-free Teflon applicable as sheets to metal (cf. Carborundum-Dielec-trix PTFE multilaminar, above). Have worked on silicone-urethane coating system for aircraft; plastics powder technology; porous metal (nickel-boron alloy) impregnated with Teflon. No literature yet furnished.

Whitford Corp.

(A-1) XYLAN Coatings, fluorocarbons in matrix of polymers (e.g. polyimides) to make a composite or "plastic alloy" of combined good properties--low friction, release, chemically inert, tough, durable, wear and weather resistant, corrosion resistant, good adhesion to metal, plastics, wood, ceramics. Application: clean (primer not generally needed), spray (as liquid in solvent, e.g. ethyl acetate or dimethylformamide, can use electrostatic spray); cure: fuse 32-40 minutes at 284-650°F (140-344°C). For best non-wetting, lightly buff with clean, dry cloth to expose fluorocarbon. Several variations suggested:

(A-1) XYLAN 1010--low friction, wear resistant, high temperature release.

(A-1) XYLAN 1014--less fluorocarbon, harder, more abrasion resistant.

(A-1) XYLAN 1052--contains EP (epoxy) lubricating solids for greater load bearing and life with low friction.

(A-1) XYLAN 8450--no info.

Zip Aerosol Products

(B-2) Zip D-5917 GP Airframe Grease, molybdenum disulfide fortified synthetic grease (MIL-G-21164 C)--Intended for open gears, cables, etc., on aircraft, for prevention of ice adhesion (FAA AD 64-9-2). Application: spray.

(C-3) Zip D-5928 Synthetic Aircraft Grease, a non-soap, synthetic hydrocarbon fluid type grease--lubricant, low wear, low lubricant drag, wide temperature range, high resistance to water washing (MIL-G-81322 A). Application: spray.

(C-3) Zip D-5082 Corrosion Control Lubricant, effective rust preventive for severe conditions, displaces water, tough, transparent, self-healing film, resists flow to 175°F (80°C), adheres firmly to metal (MIL-C-16173 D). Application: spray.

(All likely impermanent.)

APPENDIX C. Manufacturer's addresses and Contacts

Addresses of firms listed in test and Appendix B as having products of interest, with name of individual contact:

Allied Chemical Corporation
Corporate Headquarters
P.O. Box 1057R
Morristown, N.J. 07960
201-455-2000

Mr. William K. Stemple
Director, Government Sales

--Specialty Chemicals Div.
P.O. Box 1087R
Morristown, N.J. 07960
201-455-6092

Mr. Pritam S. Minhas
(Project Leader)

American Technical Industries
P.O. Box 399
Stoughton, MA 02072
617-828-4480

Mr. T.E. Gallivan
Marketing Manager

Armstrong Products Co.
P.O. Box 657
Warsaw, IN 46580
219-267-3226

Mrs. Donna L. Watkins
Customer Service Repr.

Axel Plastics Research Laboratories, Inc.
41-14 29th St.
Long Island City, N.Y. 11101
212-729-4646

Mr. B. Frank.
Sales

Cabot Corp.
125 High St.
Boston, MA 02110
617-423-6000

Mr. Kenneth A. Loftman
Marketing Manager
Cab-O-Sil Division

--Cab-O-Sil Distributors:
New England Resins & Pigments Corp.
316 New Boston St.
Woburn, MA 01801
617-935-8910

Mr. James F. Craffey

Caig Laboratories, Inc.
1175-0 Industrial Ave.
P.O. Box 64
Escondido, CA 92025
714-743-7143

Mr. Otto A. Lohkemper

PRECEDING PAGE BLANK-NOT FILMED

Carboline Co.
350 Hanley Industrial Court
St. Louis, MO 63144
314-644-1000

Mr. W. Carl Okenfuss
Technical Service Dept.

--Eastern Agent:
119 Chandler
P.O. Box 347
Back Bay Station
Boston, MA 02117
617-536-4203

Mr. Peter Nota

The Carborundum Co.
Dielectric Div.
69 Allen Blvd.
Farmingdale, Long Island, NY 11735
516-249-6419

Mr. William J. Spry
General Manager

The Ceilkote Co.
140 Sheldon Dr.
Berea, OH 44017
219-243-0700

Mr. W.A. Severance

Celanese Plastics Co.
Box 828
Greer, SC 29561
803-877-8471
803-879-2353

Mr. Phillip L. Scoville
Product Supervisor, Cargard

Contour Chemical Co.
3 Draper St.
Woburn, MA 01801
617-935-5910

Mr. George N. Fountas
Chief Chemist

Cook Paint and Varnish Co.
P.O. Box 389
Kansas City, MO 64141
816-471-4800

Mr. Steven D. Johnson
Research Dept.

Custom Compounding
Eddystone Industrial Park
Industrial Highway
P.O. Box 812
Chester, PA 19013
215-TR6-7721

Mr. Ronald B. Taylor

deBeers Laboratories, Inc.
111 So. Fairbank St.
Addison, IL 60101
312-543-5200

Dr. Franklin M. deBeers, Jr.
President

Dow-Corning Corp.
Midland, MI 48640

Mr. Don Shephard, Specialist
Government Service Marketing

Mr. G.J. Galic (re ARC)
Marketing Development Specialist
New Ventures Business

E.I. duPont deNemours & Co.
1007 Market St.
Wilmington, DE 19898
302-774-2421 (Product Info)

Public Affairs Dept. (re Teflon-P)
Central Research & Development Dept.

Mr. Charles B. Miller
Product Manager - VYDAX
Chem. Dyes & Pigments Dept.

--F&F Industrial Finishes Div.
308 E. Lancaster Ave
Wynnewood, PA 19096

Mr. George Rist, Teflon Div.
Mr. J. David Lee

--Nearby licensed applicators
for duPont's Teflon finishes:

--Precision Coating Co., Inc.
Div. of Katahdin Iron Works Corp
58 DeDonald St.
Dedham, MA 02026
617-329-1420

Mr. Ernest Anderson

--Duralectra (Parent of Precision Coatings) Mr. James Morse
Natick, MA 01760
617-237-0095

--Boyd Coatings Research Co., Inc.
Gleasondale Rd.
Hudson, MA 01749
617-562-9622

Mr. Ray MacZuba
Tech. and Sales Manager

--American Durafilm Co., Inc.
2300 Washington St.
Newton Lower Falls, MA 02162
617-969-3300

Mr. Kenneth M. Hutchins

--Applied Plastics Co., Inc.
600 Pleasant St.
Norwood, MA 02062
617-762-1881

--Dixon Industries Corp.
Penn Dixon, Westboro Div.
P.O. Box 471, Route 9
Westboro, MA 01581
617-366-8488

--Hamlin-Steven, Inc.
300 Waterview Ave.
Bridgeport, CT 06608
203-335-2195

--The Donwell Co.
130 Sheldon Rd.
Manchester, CT 06040
203-649-5375

Mr. Don Sherman

Durok Building Materials, Inc.
Hastings-on-Hudson, NY 10706
914-GR8-1923

Mr. Tony Melford

Easton R.S. Corp.
4907 Farragut Rd.
Brooklyn, NY 11203
212-629-0920

Mr. Terry Festa

Elastomer Sales Co.
Trumbull, CT 06611

Mr. Bo. Adamson

Essex Chemical Corp.
Jamestown Finishes Div.
125 Blackstone Ave.
Jamestown, NY 14701
716-665-6313

Mr. Fred A. Bristol
Market Mgr. - Coatings

General Electric Co.

--Central Research
One River Rd.
Schenectady, NY 12345
518-385-8396

Mr. Don LeGrand
(re block copolymer)

--Plastics Dept.
One Plastics Ave.
Pittsfield, MA 01201
413-494-4738

Mr. Richard Molari
(re block copolymer)

--Silicones Dept.
Waterford-Mechanicsville Rd.
Waterford, NY 12188
518-237-3330

Mr. W.J. O'Malley
Technical Marketing Specialist
Mr. James Frewin
(re silicone compounds & greases)

General Magnaplate Corp.
1331 U.S. Route 1
Linden, NJ 07036
201-862-6200

Mr. Charles P. Covino,
L.H.D., Pres.

Goodyear Tire & Rubber Co.
Research Div.
142 Goodyear Blvd.
Akron, OH 44316
216-794-4792

Mr. A.F. (Tony) Finelli

--Goodyear Aerospace Corp.
Engineered Fabrics Div.
Akron, OH 44315

Mr. J.E. Wells
Mgr. Prod. Mktg.

Groendyk Manufacturing Co., Inc.
P.O. Box 276
Buchanan, VA 24066
703-254-1010

Mr. W.R. Cash, Tech. Dir.
Mr. Joe Finer, Tech. Dir.
Mr. Hugh MacMillan (re foam)

Hauser Laboratories
5680 Central Ave.
P.O. Box G
Boulder, CO 80306
303-443-4662

Dr. Ray L. Hauser
Res. Dir.

The O. Hommel Co.
P.O. Box 475
Pittsburgh, PA 15230
412-923-2233

Mr. Archie E. Farr,
Res. Dir.
P.E. Frit Div.

Hughson Chemical - Lord Corp.
2000 West Grandview Blvd.
Erie, PA 16512
814-868-3641

Mr. Edward C. Gustin
Sales Correspondent

--Regional Sales Mgr.
Lakeside Office Park
591 North Ave.
Wakefield, MA 01880
617-245-2228

Mr. Tony Ciampa

Impact Plastics, Inc.
P.O. Drawer 12427
Gastonia, N.C. 28052
704-922-7814

MAMECO International
(The Master Mechanics Co.)
4475 E. 175th St.
Cleveland, OH 44128
216-752-4400

Mr. Richard B. Greene,
General Manager
Vulkem Sealants Div.

--Garvin Willis Co.
171 Harvey St.
Cambridge, MA 02140
617-491-3050

Distributor for MAMECO

M&H Laboratories, Inc.
2705 Archer Ave.
Chicago, IL 60608
312-842-2132

Mr. John R. Hoppe, Pres.

Miller-Stephenson Chemical Co., Inc.
George Washington Highway
P.O. Box 950
Danbury, CT 06810
203-743-4447

Dr. P.H. Deming, Tech. Dir.

Olin Chemical Corp.
120 Long Ridge Rd.
Stamford, CT 06904
203-356-2240

M. Samuel Polis, Mgr.
Urethane Technical Service

--Olin Research Center
275 Winchester Ave.
New Haven, CT 06504

Ms. Gail H. Clarke
Tech. Serv. Repr.
Non-Foam Urethanes

C.J. Osborn Chemicals, Inc.
P.O. Box 1310
Merchantville, NJ 08109

Mr. Philip J. Whiteway,
General Manager

Peterson Chemical Corp.
704 South River
Sheboygan, WI 53081
414-458-9141

Mr. Thomas M. Blattner, Chemist
Mrs. Shirley Frederick, Secy/Tres.
Mr. Robert T. Fenner

Phillips Chemical Co.
Plastics Technical Center
Bartlesville, OK 74004
918-661-6600

Mr. W.D. Powell
Mr. Dan Perry

REN Plastics
A Ciba-Geigy Co.
5656 South Cedar
Lansing, MI 48909
517-393-1500

Mr. Denis C. Smith, Dir. of Mktg.
Mr. Ron Brouwer, Product Mgr.
Thermoplastics
Mr. Elbert (Wally) Wallace

Rilsan Corp.
139 Harristown Rd.
Glen Rock, NJ 07452
201-747-3300

Mr. Chuck Fazekas
Sales Development Repr.

Skinner & Sherman, Inc.
227 California St.
Newton, MA 02195
617-890-7200

Mr. Ralph Burner

--300 Second Ave.
Waltham, MA 02154

Specialty Products Co.
15 Exchange Place
Jersey City, NJ 07302
201-434-4700

Springborn Laboratories, Inc.
Enfield, CT 06082
203-749-8371

StanChem, Inc.
East Berlin, CT 06023
203-828-6351

Sterling Lacquer Mfg. Co.
3150 Brannon Ave.
St. Louis, MO 63139
314-776-4450

Stoner's Ink (& Chemical) Co.
Quarryville, PA 17566
717-786-7355

Structure Probe, Inc.
230 Forest St.
Metuchen, NJ 08840
201-549-9350

TFB, Inc.
1900 So. Navajo St.
Denver, CO 80223
303-936-7101

Tulco, Inc.
Talbot Mills Industrial Park
Faulkner St.
North Billerica, MA 01862
617-667-9686

--Formulators for Tulco, Inc.:

--Clifford W. Estes Co.
P.O. Box 105
Lyndhurst, NJ 07071
201-935-2558

--Silobond Products, Inc.
Wilmington, MA 01887
617-658-5420

Mr. K. Berger, Adm. Asst.

Mr. Glenn S. Bayard
Technical Dept.

Mr. Roy A. White, Proj. Mgr.
Dr. Bernard Baum, Vice-Pres.
Polymers & Chemical R&D

Mr. Frank E. Flood, Tech. Dir.

Mr. P.H. Stoner

Dr. Charles A. Garber, Pres.
(Specialists in Materials
Science and Surface Analysis
(have Auger/SAM, ESCA, ISS, SIMS))

Dr. Paul R. Tully, Pres.

Mr. David Minasian, Tech. Mgr.

Mr. Thomas Kell, Tech. Mgr.

SWS Silicones, Co.
Jointly owned by Stauffer
Chemical Co. (USA) Wokker Chemie
(Germany)
P.O. Box 428
Adrian, MI 49221
517-263-5711

UNELKO Corp.
727 E. 110th St.
Chicago, IL 60628
312-468-1700

Union Carbide Corp.
230 Park Ave.
New York, NY 10017
212-551-2345

--Chemicals and Plastics
Old Saw Mill River Rd.
Tarrytown, NY 10591
212-551-2345 (NY Office)

Vita Corporation
P.O. Box 102
Roseville, MI 48066
313-293-2900

Vitek Research Corp.
50 John St.
Stamford, CT 06902
203-325-3564

Whitford Corporation
West Chester, PA 19380
215-436-0600

Zip Aerosol Products
A Div. of Mitann, Inc.
21320 Deering Court
Canoga Park, CA 91304
213-883-4700

Mr. Jack Getson, Dept. Mgr.
Mr. Arrie Korving, Silicone
Products Mgr.

Mr. H.G. Ohlhausen, Pres.

Ms. M.C. Marcuson
Res. & Devel.

Mr. Bill Vicary, Pres.

Mr. Edward Saylor
Head of Mktg.

Mr. Robert L. Trout

Mr. V.H. Berndt
Dir. of Mktg.

Appendix D. Chemical Abstracts

Here follows, in brief, digest form, listing of the 100 abstracts found of interest, including 22 especially cited in the main text. These are among 66 marked by (X) as of special interest. Significant points are underlined. In some cases a comment has been added, in brackets []. An asterisk (*) shows those referenced in this report. The listings are chronological by abstract reference; P indicates patent, R review. Anti-ice agents that work by solubility (salts, alcohols, glycols, etc.) are mostly omitted, as are thermal methods.

- 28 5900⁸ Ice removal
A.L. Th. Moesveld
(X) Chem. Weekblad 31, 170-6 (1934)
Re ice problem in rivers and canals, did tank experiments. Minute amounts of surfactants of dipole character, low sp. gr. and little solubility made ice a spongy mass of needles vs. solid clear ice without. [cf. 37, 6378⁷ P, 52 5930, 82, 158151 P.]
- 29 8407³ P Reducing adhesion of ice to airplane rubber
W.C. Geer
U.S. 2,107,593 (1935)
Non-swelling mixture, e.g. 4:4:1 pine oil, diethyl phthalate, castor oil.
- 36 2353⁹ P Aluminum tray ... for water to be frozen
C.R. Carney
(X) U.S. 2,266,353 (1942)
Includes water-repellent, adherent, flexible protective coating of baked enamel-like layer of glycerol phthalate and urea-formaldehyde condensation product.
- 37 697⁹ Shattering and cracking of ice
P.W. West
(X) Ind. Eng. Chem. 34, 1515-18 (1942)
In mfg. ice from water of low total solids, cracking was prevented by carbonating the water before freezing. The CO₂ is partially taken up by the ice, making it softer. [cf. 82 5900⁸, 158151 P].
- 37 1070⁸ Water vapor condensate on a metal surface at low temperature (<0°C)
V.A. Bazikails
Compt. rend. acad. sci. URSS 31, 333-4 (1941) (German)
Liquid film obtained as low as -36°C, evaporated when T deviated slightly. When touched, film formed ice crystals, which evaporated if T increased 1-3°. Observations are contrary to those of Awberry and Griffiths (Proc. Roy. Soc. (London) 47 216 (1935)).

- 37 3650⁸ Crystn. of ice on various surfaces under various conditions
S.S. Urazavskii, G.I. Kotlyar
Trudy Voenno-Khoz. Adad RKKA im. V.M. Molotova 1940(3),
79-87 Khim. Referat. Zhur. 4(3), 7 (1941)
Found ice form and crystal habit varied with nature of surface on which formed: on glass, solid crust; on
stearin and varnishes, individual vertical crystals; on
rosin and paraffin, crystal aggregates. Differences
attributed to relative hydrophobicity.
- 37 6378⁷ P Water-repellent coating
(X) R. Canter, H.D. Geyer (General Motors)
Brit. 548,106 (1942)
Anti-ice sticking coating for metal: mixture of high-
melting wax, a urea-formaldehyde resin, an alkyd resin
and a solvent (from coal tar) (resin content 50-90%).
- 39 567⁷ R De-icing and anti-icing progress (for airplanes)
(X) A.A. Arnhyrn
Aero Digest 46, 118-20 (1944)
Describes chemical and mechanical methods.
- 40 4824² Reduction of adhesion of ice to de-icer (rubber) surfaces
(X) D.L. Loughborough, E.G. Haas (B.F. Goodrich Co.)
J. Aeronaut, Sci. 13(3), 126-34 (1946)
.... On natural rubber with neoprene surface coat, not all
hydrophobic surfaces gave low ice adhesion. Silicones,
applied direct or formed from silanes on surface, proved
most promising. In tests on Mt. Washington, silicones
left 50% less residual ice. Tests of a silane and silicone
oil showed them effective for over 15 days of ice and high
winds; a specially treated silicone grease, for one month.
Results were confirmed further in flight tests. [cf. 43
6860^e P, 45 10440¹ P].
- 42 1365^d P Preventing ice accumulation
(X) W.E. Palmer
U.S. 2,431, 885 1947)
Partial reaction product of 1:1 glycerol/phthalic anhydride
with excess glycerol applied to surface in volatile solvent
leaving somewhat sticky surface. The free glycerol lowers
freezing point, causing water to drain off. When free
glycerol is exhausted, apply new coating. Up to 40-45%
ethanol may be used as thinner.

- 42 2038^a P Ice-preventing coating of aeroplane propellor
 *R.S. Gaugler, H.W. Guenther (General Motors)
 (X) U.S. 2,434,203 (1948)
 Coating for permanent de-icing: 75% isobutylene (av. MW 100,000), 15% chlorinated biphenyl (42% av. Cl content, 10% ketone (plasticizer). After main deicing compound applied, it may be protected by a top finish, which may be less-flexible than main coating, e.g. 85% polyisobutylene and 15% chlorinated biphenyl. The ketone plasticizer in main coat may be C₂₄H₄₄O, a cyclic ketone derivative of isophorone. Coating thickness 0.015-0.03 in. [Perhaps the benefit of the more flexible intermediate layer here is similar to the sponge rubber flexible substrate idea of J.H. Sewell - cf. (78 17171)].
- 43 2712^g P De-icing composition
 T.A. Dissel, I.L. Ferrel (United Aircraft)
 (X) U.S. 2,451,814 (1948)
 A long-chain fatty acid partial ester of sorbitan and anhydrous potassium acetate in ratio 10:1. Apply from suitable solvent to aircraft, to lower adhesion of ice; can be used at very low T.
- 43 6860^e P Reducing the adhesion of ice to rubbery surface
 E.G. Haas (B.F. Goodrich)
 (X) U.S. 2,470,772 (1949)
 Rubber compounded or coated with liquid polymeric silicone gives decreased adhesion of ice to rubber. Such product is known in the aircraft industry as the De-icer. [cf. 40 4824², 45 10440¹ P].
- 44 10451^a Effect of ultrasonic irradiation on the formation of ... ice
 C.F. Turner, A. Van Hook
 (X) J. Colloid Sci. 5, 315-16 (1950)
 Distilled water that could normally be supercooled 5-15°C crystallized immediately at -1°C when irradiated with low (but not high) cycle high power ultrasonic waves. [cf. 51 12574^a].
- 45 10440¹ P Reducing ice adhesion to rubbery surfaces
 J.M. Davies (B.F. Goodrich)
 (X) U.S. 2,567,804 (1951)
 Natural rubber coated with neoprene is humidified by damp air, then exposed to vapors of Me₂SiCl₂. The treated surface is coated with sirupy 50% solution in hexane of the heavy greasy silicone polymer "Elastomer". Ice adhesion is reduced about 96.5%. The silicone coating is also applicable to other surfaces exposed to icing: cables, ship's rigging, antennas. [cf. 40 4824², 43 6860^e P].

46 1674^a P

(X)

Surfaces having low adhesion to ice
R. Smith-Johannsen (General Electric)
U.S. 2,575,141 (1951)

To reduce adhesion of ice to various surfaces two treatments are required: (1) deposit on surface a Silicon-containing compound containing Si-bonded OH groups, (2) treatment of same with polyorganohalopolysiloxane. The Si-bonded OH groups of primer coating react with halogens of the siloxane to give a condensation reaction with subsequent formation of a thin film comprising residues of the latter compound which are oriented on the surface, thus producing an ice-resisting surface. A class of compounds which have been found especially suitable as primer coating is one embraced by the general formula $\text{Si}_2\text{Cl}_n(\text{R})_{6-n}$, where R is a univalent hydrocarbon radical (e.g. ⁿalkyl, aryl, alkaryl, aralkyl) and n is an integer from 1 to 6. Preferably, R is a CH_3 group and n at most 4.

47 1874^f P

(X)

Surface having low adhesion to ice
R. Smith-Johannsen (General Electric)
U.S. 2,617,269 (1952)

An outer coating of polymeric monochlorotrifluoroethylene (I) decreases adhesion of certain surfaces to ice in icing conditions. E.g. Water was allowed to freeze at -13°C on flat sheets of polymeric I, polystyrene "coumar" lacquer (II), silicone resin (III), polyethylene (IV) and tetrafluoroethylene (V). A thin steel bar 1/8" above test panel provided for test of shear force to break polymer/ice bond at -10°C . I gave 400 g/cm^2 (0.39 atm, 5.69 psi, 39.2 kPa), II 2000 g/cm^2 , III 1800, IV 1900, V very erratic, poor results. In addition to its low adhesion and flexibility well below 0°C , I is flame resistant and does not support combustion. The coating may be applied to aluminum, brass, steel, wood, glass, plastics, e.g. on household, ski, auto and aircraft equipment.

47 4526^c P

Ger. 812,334 - see CA 46 1674^a.

50 1238^e P

(X)

Water-free optical surfaces
D.F. Stedman (to Hon. Advis. Council for Sci. & Ind. Res., Canada)

Can. 485,663 (1952)

Windshields, windows, etc. cleaned with celite, rubbed with an alkyl- or aryl-substituted polysilicane (I) paste, cleaned with xylene and waxed. The repellent finish is optically clear, long-lived, immune to light, sun, weather oil and de-icing damage, and is cleanable. May be applied up to 125°F (52°C). From 0 to -40°C , use alkanols for cleaning. Cloths used must be vapor-degreased after washing

and drying, with methanol or ethanol-benzene mixture. The preferred silicanes are: hexa-ethyl (I) (cheapest, satisfactory), hexabutyldisilicane (almost optimum), tetraheptyldiethy (very best but more expensive). A typical paste: I 50 g, carbon black 50 g, petroleum naphtha 400cc. A preferred wax coating: bleached amorphous mineral wax 27.5, paraffin wax 35.5, reprecipitated polyisobutylene 3.5, petroleum naphtha (BP 160-200°C) 170 parts. By use of only 10 parts naphtha, can be formed into sticks.

- 50 16131^c
(X) Cellulose lacquers - de-icing lacquer for stationary aircraft C.J. Rolle, W.B. Barnes, Jr. (Interchem. Corp.)
Ind. Eng. Chem. 48, 1326-27 (1956)
Lab development led to optimum formulation. Best lacquer film contained 1.5% silicone oil and 0.5% microcryst. wax in addition to usual film components.
- 50 17402^h
(X) Development of a lubricant
H.R. Baker, V.G. Fitzsimmons, C.R. Singleterry
NLGI Spokesman 20(6), 20-2, 24 (1956) Developed low-torque, semi-fluid grease, which is compatible with oil-resistant rubber and which resists the anchorage of ice.
- 51 12574ⁱ
(X) Crystallization of supercooled water by ultrasonic radiation
W.C. Swinbank
J. Meteorol. 14, 190 (1957)
Ultrasonic vibration stimulates freezing of supercooled water droplets of 10 μ radius (20 μ dia.). [cf. 44 10451^a].
- 51 14372ⁱ
The freezing of water droplets
A.E. Carte
Proc. Phys. Cos. (London) 69B, 1028-37 (1956)
Microscope method to study freezing of small drops condensed on surface covered with silicone oil--nickel, gold, silver. Lowest freezing T is independent of surface but depends on volume of drop and rate of cooling. Homogeneous nucleation occurs in the lowest freezing droplets. Value of surface free energy for water/ice is calculated. There is no sudden large increase in nucleation rate near the well-known transition region of water droplets near -40°C.
- 51 15204ⁱ
The surface free energy of ice
A.V.S. deReuck
Nature 179, 1119-20 (1957)
Calculated by using Rowlinson model of the water molecule - see 45 7395^g.

- 51 17265ⁱ Ice adhesion apparatus and test method
H. Lachs, M. Quantinetz, A. Freiburger (N.Y. Naval Shipyard)
ASTM Bull No. 224, 48-50 (1957)
For coatings of little or no ice adhesion.
- 52 4071^d p Coatings for simplifying frost removal from refrigerated
surfaces
(X) R.H. Goms
U.S. 2,812,264 (1957)
Non-toxic taste and odor-free coating giving only poor
adhesion of frost to cold surfaces, still effective after
five defrosts, readily applied by wiping. Typical com-
position: peanut oil 79.17, coconut oil 4.17, Witco
aluminum stearate 3.33 and propylene glycol 10%. Other
vegetable oils and water-insoluble ateates of Mg or Ca
may be substituted. Also satisfactory was: white mineral
oil 70.5, oleic acid 9.0, stearic acid 1.5, slaked lime
(Ca(OH)₂) 3.0, CaCl₂ 15.0, and water 1%. Effects of
aluminum stearate and of propyleneglycol on frost
adherence were determined. Tables give expected life
of various vegetable oil coating compositions based on
average adhesive force after 1-5 operations.
- 52 5061^c Effects of certain chemicals on the inhibition of nucleation
(X) S.J. Birstein (AF Cambridge Res. Ctr.)
Artif. Stim. Rain, Proc. Conf. Phys. Cloud Pptn Particles,
1st, Woods Hole 1955, 376-85 (publ. 1957)
Expts. showed nucleation of ice can be inhibited by chemi-
sorbing traces of NH₃, sec BuNH₂, ethanol, MeNH₂, and EtNH₂.
Isobutene, ether, heptane, PhBr and glycol were unable to
inhibit nucleation at -20°C. In the atmosphere nucleation
was inhibited by EtNH₂ at -40°C. The mechanism of this
inhibition is the formation of metal-amine complexes on the
surface of the nucleating agent. [cf. 83 208580].
- 52 5089^c Adhesive and cohesive properties of ice when used as an
adhesive between solid surfaces
J.V. Laukonis (U. Cincinnati)
U. Microfilms, No. 24797, 117 pp., Diss. Abstr. 17, 3056
(1957)
- 52 5930ⁱ Experiments about adhesion forces of ice to solids
(X) L. Vahl (Tech. U., Delft, Neth.)
Congr. Intern. Froid, 9th, Paris, 1955
Compt. rend trav. comm. I et II, 2011-18 (English)
In expts. in which force of adhesion was measured by
pressing a conical core of ice from a tapered specimen,
found: (1) stainless steel, Monel and chrome have lower
adhesion than steel, (2) surfactants dissolved in water

before freezing lower adhesion substantially, (3) roughness affects the force, but for the usual types of machine finishes it is of less effect than the kind of metal. [Perhaps (1) is because such steels may have less oxides and hydroxide oxidation products at the surface than ordinary steels, hence less H-bonding. Regarding (2), cf. 28 5900⁸ and 82 158151 P, where surfactants in water made ice softer; also, Sayward (1963) found dry surfactants mixed in made compressed snow weaker.]

52 17866ⁱ

(X)

The adhesion and strength properties of ice
*L.E. Raraty, D. Taber (Cambridge U., England)
When water is frozen onto clean metal the interface is stronger than the ice and fracture occurs within the ice, as shown by stainless steel. Failure can be brittle or ductile according to the stress value. Surface contamination reduces the adhesion by a large factor. Adhesion of ice to polymeric materials is different from metals, interface strength being less than strength of ice. Data are given for PTFE, solid stearic acid, polystyrene and perspex. Creep rates are studied. Study bears on deicing of ships and aircraft, and procedures are proposed.

52 19316^e

(X)

Strength characteristics of ice
S.G. Eskin, W.R. Fontaine, O.W. Witzell (Purdue)
Refrig. Eng. 65(12), 33-8, 52 (1957)
Several techniques and pieces of apparatus were integrated to determine the strength of ice and the forces of adhesion to various surfaces. Measurements made by pulling specimens vertically from a vertical or horizontal test surface. Initial water T, water freezing T, ambient test T and ice-test surface contact area were held constant. Actual force necessary for failure in ice was recorded and correlated for the different materials: brass, black Teflon, white Teflon, stainless steel, aluminum, anodized aluminum, anodized and rewaxed aluminum, de-icing lacquer-coated brass, polyethylene, hardened steel.

53 9692ⁱ P

(X)

Ice releasing coating compositions
C.J. Rolle, J. Rotamen, W.D. Barnes, Jr. (Interchemical Corp.)
U.S. 2,872,422 (1959)
Coating compositions: nitrocellulose 10, vegetable oil-modified glycerol phthalate 10-20, copolymer of vinyl chloride and acetate 2.5-5.0, petroleum wax 0.1-0.3 parts and solvent to impart sprayability. Coatings especially useful on aircraft to prevent collection of thick layers of ice.

53 15702^e

(X)

Adhesive properties of ice
*H.H.G. Jellinek (SIPRE)
J. Colloid Sci. 14, 268-80 (1959) cf. CA 51 1684^a
Artificial snow-ice was mounted between stainless steel disks at -10°C and the strength of the compacts tested as

$f(T)$ under shear or tension. Breaks under shear occurred by cohesive failure below -13°C . Above this, adhesive failure occurred, strengths being a linear $f(\Delta T)$ below FP . The same type of linear relation to T was observed with ice between polystyrene disks, with limiting T -15°C under shear, -25.5°C under tension. Expts. with ice between PMMA (polymethylmethacrylate) at -5° indicated adhesive strength to ice greater than for PS (polystyrene). Results are explained by assumption of liquid-like layer between ice and disk, its thickness and consistency being a $f(T)$ and nature of interface. [cf. 61 37168].

54 8108^h

(X)

Effect of organosiloxane coatings on the adhesion of ice to different surfaces

K.A. Andrianov, B.V. Deryagin, N.N. Zakhavaeva, M.V. Sobolevskii, M.V. Talaev

Zhur. Priklad. Khim. 32, 2682-91 (1959)

Adhesion of ice to rubber, plastics and aluminum surfaces coated with varnish was reduced by application of a film of Me, Et or iso-Am polysiloxane. Its effect on glass and aluminum surfaces without a preliminary coating of varnish was low.

54 8254^a (53¹) Theory of metastable phase transformations

L.S. Palatvik, V.S. Zorin

Zhur. Fiz. Khim. 33, 1859-65 (1959)

... The surface tension of ice, $\alpha_{ice} = (0.97 \pm 0.02) \times (\alpha_{H_2O})$ was calculated from data on stepwise condensation of water vapors supercooled to below 0°C ...

55 12972^f R

(X)

Mechanism of adhesion between solids

F.P. Bowden, D. Taylor (U. Cambridge, England)

Proc. Int. Conf. on Surface Activity, 2nd, London, 1957, 3, 386-97

Review of reported work, discussing the thermodynamics of adhesion, adhesion of ice to solids, and the adhesion of metals in contact with other metals, 9 ref.

55 15058^b

(X)

Wettability of perfluorocarbon polymer films: effect of roughness

A.J.G. Allen, R. Roberts (duPont)

J. Polymer Sci. 39, 1-8 (1959)

The advancing and receding contact angles formed by a drop of liquid on a surface were used to study the wettability of various perfluorocarbon polymer surfaces. Variations in roughness changed the advancing angle by as much as 30° , and the advancing-receding hysteresis varied $13-59^{\circ}$. The receding angle is probably the more important one in the

adhesion of ice where drops are blown across the surface at glancing angles and, therefore, exceedingly smooth perfluorocarbon polymer surface may be better than rough for this application. No significant difference was observed between poly(tetrafluoroethylene) and the copolymer of C_2F_4 and C_3F_6 .

56 6683^c

Thermal expansion of ice

S. LaPlaca, B. Post (Brooklyn Polytech.)

Acta Cryst. 13, 503-5 (1960) (English)

Measured by x-ray diffraction and dilatometry down to $-250^{\circ}C$; some inconsistencies about $-180^{\circ}C$... Randomly oriented crystals from spraying fine mist onto cooled glass not satisfactory for diffraction until tempered by heating just below MP and cooling slowly gave desired orientation.

56 8089^e

Requirements of an ice nucleus

G.R. Edwards, L.F. Evans

(X)

Nature 192, 448-9 (1961)

Efficiency of nucleating agent discussed--gives exptl evidence that ice nucleation is a function of the surface charge of the nucleating substrate. Nucleation is most efficient in vicinity of isoelectric point, and extreme supercooling is required when surface is charged either pos. or neg. [Perhaps, then, on a charged surface supercooled drops might run off without or before freezing.]

56 12382^e

Low temperature cloud chamber studies on water vapor

L.A. Madonna, C.M. Schulli et al (U. Ottawa)

(X)

Proc. Phys. Soc. (London) 78, 1218-22 (1961)

Critical supersaturation for pptn. of water droplets or ice crystals from vapor was measured, 0 to $-75^{\circ}C$, by expansion chamber technique, with N_2 as carrier gas.

Temperature dependence of critical supersaturation was same in presence or absence of electric field. Latter probably heterogeneous nucleation on ions... Pptd. particles spherical above $-65^{\circ}C$, isomorphous ice crystals below.

57 6654^h

The adhesion of ice to lubricated surfaces

W.D. Bascom, C.R. Singletary (USNRL)

(X)

J. Colloid Sci. 17, 477-91 (1962)

Measurement of water contact angles and force of detachment of ice buttons from steel and Teflon surface under oil show that the adhesion of ice to lubricated steel varies widely, depending on polar organic additives in the oil. Adhesion is least for systems of contact angle 170° or larger through water drops on the submerged steel. The very low adhesion sometimes observed in such systems arises because water does not readily displace the final thin film of bulk

oil from the metal surface for true water/solid contact. However, long contact times of water and surface before freezing, or low viscosity of oil phase, contribute to more complete oil displacement and stronger adhesion. High water contact angles are associated with strong adsorption of the polar additive at the oil/metal interface and with relatively low adsorption in the oil/water interface.

57 12661^B P

(X)

Surface layers and methods of applying viscous liquids to surfaces

J. Currant et al

U.S. 3,038,822 (1962) Parts of aircraft exposed to atmosphere given improved surface layer highly resistant to rain, ice, etc: mixture of an epoxy resin (epichlorhydrin and Bisphenol A) and stainless steel particles 10-70 μ , hardness Rockwell B30 to C62. Mixture is 80-93% metal powder. Protective layer is especially useful to cover an electric surface heating element on leading edge of wing. The viscous fluid mixture of resin and metal powder is applied to an upper part of the surface which is then preferably vibrated in horizontal direction. Heat is applied to fluid and/or surface during vibration. The flow of fluid over the surface may be assisted or controlled by a stream of gas (maybe warm). U.S. 3,038,823: Additional claim wherein applied vibration is ≥ 40 Hz.

60 6660^B

(X)

Ice nucleation by hydrophobic substrate

A.C. Zettlemoyer, N. Tcheurekdjian, C.L. Hosler (Lehigh U.)

A. Angew. Math. Phys. 14, 296-502 (302-?) (1963)

Active ice nucleating surfaces which might be used for cloud seeding are expected to be predominantly hydrophobic with isolated polar sites. The surfaces of fine particle precipitated silica were made hydrophobic by heating to $\geq 650^\circ\text{C}$ and were further modified by adding e.g. AgNO_3 , PbI_2 , ZnCl_2 . Some of these samples showed exceptional activity in lab tests.

60 8967^d

(X)

Special silicone treatments of anodized aluminum surfaces

Y. Tsuji

Trans. Inst. Metal Finishing 40(5), 225-8 (1963)

Application of special organic siloxane to anodized aluminum surface is followed by heat treatment in a new process for reducing adhesion of ice to aluminum alloy used in refrigeration. Poly (methyl, ethyl and phenyl hydrosiloxanes) are applied as 10% solutions in petroleum ether-benzene, methanol-benzene, and butanol-benzene, resp. Heat treatments were steam sealing in aclave at 50 psi for 25 min., heating in air oven at 110°C 30 min., and sealing in water near BP for 30 min., then heating at 140°C 25 min. Coatings were

examined for abrasion and corrosion resistance. Treatments were more effective with 2S alloy than for 3S. Abrasion resistance was increased about 10-fold and it is considered that this improvement results from chemical bonding between organic hydrosiloxanes and anodized layers.

61 3716^g

(X)

Liquid-like layers on ice
H.H.G. Jellinek (Assumption U, Windsor, Can.)
J. Appl. Phys. 32(9), 1973 (1961)
The adhesion properties of ice were measured. Tensile and shear expts with ice between disks of stainless steel, various polymers, and quartz optical flats gave results comprehensible only by assumption of a liquid-like layer for the ice interfaces. Reasonable estimates of its thickness and viscosity, assuming it Newtonian, were made - for -4.5°C giving thickness about 10^{-5} - 10^{-6} cm (0.1-0.01 μ) and viscosity 70-100 poise for ice/stainless, 15-150 poise for ice/quartz. Shear with water films of 0.2-0.1 μ thickness between optical flat glass plates showed characteristics very similar to those obtained with ice. T. Hori (1956) reported that water films of 1.3 μ between glass plates demonstrated abnormal VP and FP and did not freeze even at -96°C. [cf. 53 15702^e].

62 5184^e

Synthesis of C₁₀ dicarboxylic acids from 1.3 butadiene, Na and CO₂
P.A. Moshkin et al (USSR)
Sintez i Svasttva Monomerov, Akad. Nauk SSSR, Inst. Neftekhim, Sinteza, S. Rabot 12-oi (Dvenadtstoi) Konf. po Vysokomolekul. Soedin. 1962, 212-15 (publ. 1964) (Russian), cf Plastmassy 1962(7), 59
A synthesis is described leading to a product which when applied to a poly(chlorovinyl) film gives a product resistant against frost at -50°C.

62 8712^g P

Werner complexes of Cr⁺⁺⁺
A.A. Bartz (duPont)
Fr. 1,374,783 (1964) (US Appl. 11/15/62)
Viscous blue complexes suitable for weatherproofing paper and textiles and de-icing glass, not requiring high T hardening, and which may be neutrallized to pH 4-5 without decomposition, are made by reaction of Cr(OH)Cl₂ dissolved in an alcohol with ≤ 4 C atoms with an aliphatic monocarboxylic acid having a solubility of $< 0.1\%$ in water at 20°C. No more than 6% water is added to a total of 8-50% and the mixture warmed to 35-70°C for 20-75 min. Thus, 514 parts anhydrous chromyl chloride is introduced under the surface of 1928 parts boiling isopropanol. After 45 min. of refluxing in a nitrogen atmosphere, the chromyl chloride is reduced to Cr(OH)Cl₂ and the mix cooled to 50°C. Then

379 parts myristic acid is added and the mix held at 40° for 70 min., 180 parts water added, and T held at 40°C for another 30 min. The clear blue solution contains Cr 5.75% and water 9% and has a Cr:acid mol ratio 2:1, density of 0.9399, viscosity 8.59 cp at 30°C. A 1% aq. solution neutrallized to pH 5.0 with NaOH is used to waterproof paper.

63 801^d P

(X)

Ice-proofing surfaces, such as glass, by treatment with silicone polymers

J.W. Kiel, C.L. Whipple (Dow-Corning)

Fr. 1,381,590 (1964) (US appl. 12/3/62)

Surfaces that resist ice formation are produced by applying a solution of a polymer $(\text{HO}(\text{Si}(\text{CH}_3)_2\text{O})_x)_3\text{Si}(\text{R O}(\text{CH}_2)_3\text{NHQ})_n$, in which $x = 10-400$, $n = 0-3$, R is a C_{3-7}^x alkyl, and Q is H, CH_3 or $(\text{CH}_2)_2\text{NH}_2$, in suitable solvent such as ethanol, methanol or isopropanol. Thus 20 g hydroxylated poly(dimethylsiloxane) containing 3.5-4.5% OH groups, 1 g $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$, 1.2 g acetic acid, 20.8 g isopropanol reacted to produce an isopropanol solution of $(\text{HO}(\text{Si}(\text{CH}_3)_2\text{O})_{12})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$. This solution is applied to glass and dried to produce a surface resistant to formation of ice.

64 4350^c

(X)

The sintering and adhesion of ice

P.V. Hobbs, B.J. Mason (Imperial College, London)

Phil. Mag. 9(98), 181-97 (1964)

Current theory of sintering is incomplete and so present experiments on sintering ice are misinterpreted. Evaporation-condensation theory is now extended to the case where material is transferred by diffusion through an environmental gas. Measurements were made on rates of growth of the neck formed between single and polycrystalline ice spheres 50-700 μ dia in range -3 to -20°C in air at 1 atm. Results are in quantitative agreement with new evaporation-condensation theory, and further confirmation was obtained from expts. with spheres of heavy ice, and by observing effects of replacing air by either hydrogen gas or silicone oil. Sintering of ice by either volume or surface diffusion would be slower by almost 4 orders of magnitude. No evidence is found for the recent suggestion that the sintering and adhesion of pure ice is caused by the existence of a liquid-like surface layer. The ice spheres show symptoms of having such a liquid layer only if they contain dissolved salts or if their surfaces are otherwise contaminated.

68 13619

Studies of ice adhesion. I. Adhesion of ice to plastics

*M. Landy, A. Freiburger (USN Appl. Sci. Lab, Brooklyn)

J. Coll. & Interf. Sci. 25(2), 231-44 (1967)

Ice adhesion (stress to separate block of ice from substrate) was determined at -12°C for 29 rigid plastics. All were adhesive failures (no ice left on plastic). Adhesion did not correlate with γ (critical surface tension) of wetting, contact angle, thermal conductivity or expansion, porosity, dielectric constant and flex modulus. However, when plastics of same thickness were grouped by types of chemical bonds they formed with ice, the ice adhesion in each group increased with the flex modulus. Addition of pigments and fillers to polymers increased adhesion. Polymers used were Teflon FEP, Lexan, Teflon TFE, Plaskon CTFE 2200, polyethylenes (Seilons ETH and ETH-R, Alathon 10, DYDT, Epolones C-10, N-10 and N-11, and CA 1220), nylon 66 (Zytel 101), ABS copolymer (Seilon S-3), acetal (Delrin), polypropylene (Seilon PRO), polyvinylidene fluoride (Kynar), polymethylmethacrylate (Plexiglas), epoxy (Bakelite ERLA-2256).

68 96849

(X)

An approach to the shipboard icing problem

*M. Landy, A. Freiburger (USN Appl. Sci. Lab)

Nav. Eng. J. 80(1), 63-72 (1968)

Ice adhesion test methods, deicing coatings, and environmental factors that affect ice adhesion are discussed. Ice adhesion generally increases with increased interfacial area, freezing rate, water purity, age of ice-substrate joint, and stress application, and with decreased test T. Of 40 coatings tested, the lowest ice adhesion (4-5 psi) was to certain silicone coatings, e.g. Dow-Corning XZ-8-3057.

70 61936

Morphological stability and the ice-water interfacial free energy

S.C. Hardy, S.R. Coriell (NBS)

J. Cryst. Growth 1968 (3-4), 569-73

Growth rates of slightly perturbed single crystal ice cylinders with (0001) orientation in supercooled water were measured. By using the morphological stability theory, the ice-water interfacial free energy was calculated from exptl observations-- 0.016 J/m^2 (16 ergs/cm^2), which is an average value for planes parallel to (0001).

71 95123

Experimental determination of surface energies of ice

W.M. Ketcham, P.V. Hobbs (U. Washington)

Phil. Mag. 1969 (19), 1161-73

A direct exptl method was used to determine the magnitude of ice/ H_2O vapor, ice/ H_2O liquid, and ice/ice (grain boundary) surface free energies, i.e. 109, 33 and 65 ergs/cm^2 resp. at 0°C . Results indicate grain boundary free energy varies slightly with mismatch between grains but that variation with the

liquid surfaces are small.

- 71 102840 P Water repellent and/or release treatment
J.W. Keil, C.L. Whipple (Dow-Corning)
(X) U.S. 3,460,981 (1969)
A silicone copolymer salt facilitates ice release, with no effect on glass visibility. Examples show 6 psi release value of ice from steel, < 3 psi from glass.
- 71 103886 R Atmospheric icing of structures
D.W. Boyd, G.P. Williams
NRC Canada, Div. Bldg. Res., Tech. Paper 1968, No. 275, 10 pp. (25\$)
Literature on atmospheric icing is reviewed. Types of ice formed are classified as hoarfrost, rime and glaze. Conditions of formation are discussed. A possible general approach to control and prevent them is outlined. 18 ref.
- 72 25378 Ice adhesion to hydrophilic and hydrophobic surfaces
W.D. Bascom, R.L. Cottingham, C.R. Singletary (Chem. Div., NRL, Wash.)
J. Adhes. 1969, 246-63
Adhesion shear strength was determined for ice formed against polished steel, monolayers adsorbed on steel, and thin plastic coatings painted on metal. The adsorbed monolayers reduced shear strength to about 1/2 that of ice on clean steel. Monolayers also changed the character of the break from clearly cohesive to apparently adhesive failure. The shear strength from plastic coatings ranged from same as steel to 70-80% lower. Reduction in shear strength did not correlate with water contact angle on coatings but was usually found due either to air entrapment* at the interface or to cohesive failure of the coating itself. The ice separated from the various substrates was examined microscopically by forming plastic replicas of the ice surface. These studies helped determine the mechanism of failure and since one of the replicating solutions was also an ice etchant, much was learned about the crystal structure and the crystal defects of ice near surfaces. The ice lattice was highly defective near the substrates, and this is discussed in connection with the "liquid-like" behavior of interfacial ice.
- *The entrapment of air at an ice/water interface may be a factor in frost action as well as ice adhesion. In earlier work (Sayward 1967, 1969) an adhering air layer appeared to be a factor in the rejection of certain nylon balls by slowly freezing ice, whereas other plastics were engulfed. They showed the "gaseous plastron" effect (like the silvery appearance of some plant leaves, insects and feathers in nature upon immersion, due to air being held by the waxy, perforated or fibrillated hydrophobic surface). Such effect also is noted by Tulco, Inc. for coatings containing their Tullanox (hydrophobed pyrogenic silica)--see Survey of Manufacturers in text.

- 72 115443 Interfacial phenomena associated with freezing of water
W.M. Ketcham, Jr. (U. Wash.)
1968, 131 pp, Univ. Microfilms, order 69-13, 573
From Dissert. Abs. Int. B 1969 30(2), 784
- 72 123641 Adhesive shear strength of ice to bonded solid lubricants
(X) *J.R. Jones, M.N. Gardos (R&D Div., Hughes Aircraft)
Mater. Processes '70's, Nat. SAMPE (Soc. Aerosp. Mater.
Proc. Engrs.), Symp. Exhibit, 15th 1969, 1021-9
The adhesive shear strength of ice to solid surfaces, which
is directly related to surface roughness and porosity, was
tested using unfilled and lubricated coatings. Phenolic-
bonded solid lubricant containing MoS₂ had ice adhesion
like bare steel; addition of fluorinated copolymer of CH₂:CH₂
and CH₃CH:CH₂ (I) to coatings increased adhesion without
increasing normal cure T. Coatings based on silicone resins
(II) and polyimide resins (III) cured at $\geq 500^{\circ}\text{F}$, containing
I lubricative filler, had much lower adhesion to ice than
phenolic coatings (per MIL 8937). Adhesion to sandblasted
steel increased linearly with decreasing T to -65°F . The
I-III coating had a good wear life, i.e. about half that of
a typical MIL 8937 material under same conditions, while
I-II coatings had poor wear life. Curing II- and III-based
coatings at 300°F rather than normal 500°F greatly reduced
wear life.
- 73 29669 Existence of a quasi liquid film on the surface of ice
(X) *V.I. Kvlivdize et al (USSR)
Dokl. Akad. Nauk SSSR 1970, 191(5), 1088-90 (Russian)
The frost formed by liquid nitrogen on walls of a Dewar
was investigated by NMR. Spectra had two components--
wide and narrow. The narrow was clear at $\geq 268^{\circ}\text{K}$ (-5°C)
and its intensity increased with T. A weak narrow component
was also observed from polycrystalline ice from freezing
water in an ampule. The wide component is produced by
rigidly fixed molecules in the crystal lattice of ice,
whereas the narrow is produced by labile water molecules
or protons. A curve for the content of narrow component
vs. T extly agrees qualitatively with the curve derived
theoretically by N.H. Fletcher in 1963. This again indicates
that the narrow component of highly dispersed ice is due to
labile water molecules forming a quasi-liquid film on the
solid ice crystal. A rough estimate of the correlation
time τ_c of the labile molecule by the theory of relaxation
gives τ_c about 10^{-8} , whereas for ice τ_c is about 10^{-4} and for
water about 10^{-11} . This value for τ_c is very near that
for water adsorbed on silica gel. [cf. 74 57997, 81 84083,
82 47973 R, 82 47974 R, 82 145634].

73 91707

Experimental measurement of solid-liquid interfacial energies of transparent materials

D.R.H. Jones, G.A. Chadwick

Phil. Mag. 1970, 22 (176), 291-300

Exptl. γ_{SL} for the system ice/water, white phosphorus, camphor, succinonitrile resp. were: 41 (avg. over planes containing c-axis), 10.5, 5.3, 28 ergs/cm² (10^{-3} J/m²).

Results were derived by direct observation of shapes of grain-boundary grooves at a solid/liquid interface in a thin sample in a T gradient. The anisotropy of γ_{SL} in the three latter substances was small.

74 15987

Contact angles on molecular solids. I. Ice

*A.W. Adamson et al. (U. So. Calif.)

J. Coll. Interf. Sci. 1970, 34(3), 461-8

Advancing contact angles on flat polycrystalline ice were measured for a number of liquids at -5°C. Depending on which series of liquids was used, the critical surface tension of ice was about 29 or 40 dynes/cm. The advancing contact angle for CS₂ on basal plane of single crystal ice is also given, -5 to -50°C, showing a constant T coef. of 0.35. A contact angle of 42° at -5°C suggests the ice surface is liquid-like, but linear T dependence suggests no point down to -50°C for change to rigid surface structure. These two sets of apparently dichotomous behaviour as well as that of ice as an adsorbent for vapors are explained in terms of whether or not a given liquid or adsorbed vapor restructures the ice surface in the T range where it is mobile. Class A liquids, which include CS₂ and halobenzenes, are inert with respect to such action, whereas Class B, which includes alkanes and Cl alkanes, are surface restructuring. The distinguishing features of Class A and B liquids are discussed briefly.

74 57029 P

(X)

Composition for the formation of a coating for airfields, roads and similar installations

K.N. Andrushshak et al

USSR 280,517 (1970)

From Otkrytiya. Isobre, Prom. Obraztsy. Tovarnye Zuaki 1970, 47(28), 34.

Based on waterglass, blast furnace granulated slag (BFGS) and sand. To lower the adhesion of ice to the surface, clay 5-25 and an aq. solution of alkali metal ion 5-12% were added to the composition of water glass 2-4, BFGS 21-31, and sand 35-60%.

74 57997 R

(X)

Possible existence of a quasi-liquid film on the surface of ice crystals at sub-zero temperatures

L.A. Ushakova, V.I. Kvlividze, A.A. Sklyauken (USSR)
Svyazannaya Voda Dispersnykh Sist. 1970, No. 1, 155-66
(Russian)

Starting from the hypothesis based on there being a movable liquid film on the surface of ice crystals, all available theoretical and exptl works on surface properties of ice at $< 0^{\circ}\text{C}$ are reviewed. Anomalous properties probably result from the high-dispersion state of matter. Some direct methods such as electron diffraction, IR spectrometry and NMR are proposed for determining structure and properties of quasi-liquid films. Recent applications of NMR are also discussed. 34 ref. [cf. 73 29669 et al.].

74 68099

Experiments on the contact angle of water on ice
C.A. Knight (NCAR, Boulder, CO)

Phil. Mag. 1971, 23(181), 153-65

Results of two new expts to determine contact angle of water on ice: In one, the first stage of melting of a clean ice surface is liquid formation at discrete sites, not uniformly as predicted if contact angle zero. Water has a downward meniscus and sharp contact angle against ice both melting and freezing. In the second expt., ice disks are grown in water at approx. 0.010°C supercooling, and contacted by air bubbles on their smooth, basal faces. According to this expt, the contact angle of water on ice is zero. These contradictory results may be the result of anisotropic surface energy or an effect of disequilibrium.

76 18101

Hydrophobic surfaces

*A.C. Zettlemoyer (Lehigh U)

Hydrophobic Surfaces, Kendall Award Symp. 1968 (publ. 1969), 5, 1-27, Ed. by E.M. Fowkes, Academic Press

Review (64 ref), including discussion of contact angle formed by a liquid drop on a solid surface not wetted by the liquid, measurement of heats of immersion, nature of interfacial tension, determination of dispersion part of surface free energy of solids, spreading pressures on hydrophobic surfaces, and surface properties of ice nucleants.

76 50892

Experimental measurement of solid-liquid interfacial energies. Ice-water-NaCl system.

D.R.H. Jones, G.A. Chadwick (Cambridge U., England)

J. Cryst. Growth 1971, 11(3), 260-4

Devised direct method for measuring change in γ_{SL} of impure transparent materials caused by addition of solutes.

Method illustrated by measurements in ice-water-NaCl

system for NaCl concentrations 0-1.00 M. γ_{SL} increased linearly with increased solute concentration-- γ_{SL} for 1.00 M was about 13 ergs/cm² greater than for pure water.

76 127910

(X)

Adhesion of ice to some plastics

V.I. Gritsai, A.I. Nechipor et al (USSR)

Teor. Eksp. Isaed. Uslovii Obledenenuja Sudov 1971, 146-9, Ed. by E.P. Borisenkov, Gridometeorol. Izd., Leningrad, USSR

The adhesion FORCE of ice to 10 plastic surfaces was lower than that to steel and aluminum at -20 to -5°C. Force increased with decreasing T and was lowest for polyethylene (PE), polyvinyl chloride (PVC), and Viniplast.

77 9998 R

The ice interface

H.H.G. Jellinek (Clarkson Col.)

Water and Aqueous Solutions: Structure, Thermodynamics, Transport Processes 1972, 65-107, Ed. by R.H. Horne (Interscience)

Summary of properties of ice interface, including the ice/water liquid interfacial free energy, interfacial ice transition layer, ice growth and diffusion, surface conductivity, freezing potentials, ice growth habits, vapor adsorption on ice surfaces, contact angles, and water structure near macromolecules.

78 17171

(X)

Development of an ice-shedding coating for helicopter rotor blades

*J.H. Sewell (Roy. Aircr. Establ., Barnborough, England)
US NTIS AD Rep 1971, No 746784, 25 pp.

The adhesion of ice to a low energy surface film on a rigid base was reduced by using a sponge rubber substrate between the surface and the base, e.g. of helicopter blades.

78 31121

(X)

Friction of polymers on ice

W. Gnoerich, K.A. Groseh (Uniroyal, Germany)

J. Inst. Rubber Ind. 1972, 6(5), 192-6 (English)

Frictional behavior of natural, butyl, nitrile and SBR rubbers on contaminant-free highly polished ice at -5°C can be predicted from master curves for glass (WLF transformation). Filling rubbers with carbon black lowered friction coef., whereas oil extension of carbon black filled rubbers increased it. Blending of carbon-black filled or unfilled rubbers increased and broadened the region of high friction of the blend to cover the high friction areas of both compositions. [cf. 83 44464, 84 45716].

78 112044

(X)

NMR study of a frozen, strongly hydrophobic Floroplast-3 $[(C_2ClF_3)_x]$ Suspension
A.B. Kurzaev et al (USSR)
Dokl. Akad. Nauk SSSR 1973, 208(2), 391-3 (Russian)
Difference in widths of NMR lines given by relatively immobile water molecules inside ice crystals and the mobile water molecules on the ice surface provided a method for determining specific surface at the ice- $(C_2ClF_3)_x$ interface. During storage of ice- $(C_2ClF_3)_x$ dispersions at 265°K (-8°C) the fractions of the least mobile and of the most mobile water increase at the expense of water molecules of average mobility. Below 273°K (0°C) there is a liquid-like mobile layer at the ice $(C_2ClF_3)_x$ interface. The mobility of protons inside ice crystals increases when the crystal sizes are decreased.

[Could such liquid-like layer actually increase adhesive strength by not cracking and not allowing access of air upon separating, as compared to adhesion with no such layer, i.e. solid-solid? JMS 6/13/771

80 31103

Free surface energy of solid compounds, especially oxides, in the unrelaxed state as dependent on temperature
H.H. Wawra (E. Ger.)
Radex Runsch. 1973 (4), 602-21 (German)
Surface free energy of many oxides, also H_2O (ice) was determined as a function of T and P by sonic-ultrasonic method. Values obtained are upper limits for release time=0, thus giving a basis for comparison of data between solid and liquid phases and for correction of numerical results of previous investigation...

80 74540

Calculation of surface free energy components of ice by its wettability by water, chlorobenzene and CS_2
J. Kloubek (Czech.)
J. Col. Interf. Sci. 1974, 46(2), 185-90 (English)
Dispersion and polar components of the surface free energy of ice were calculated, using the principle of additivity and geometric mean of similar forces interacting across the interface of contiguous phases. Comparison shows qualitative differences between ice and water surface, ice predominantly non-polar. The surface tension components of chlorobenzene and CS_2 were evaluated by the same method and their spreading pressures on ice computed. Both form autophobic adsorbed layers which change the nature of the ice surface.

- 81 84083 Mobile water phase on ice surfaces
V.I. Kvlividze et al (USSR)
Surf. Sci. 1974, 44(1), 60-8
NMR spectra of finely dispersed ice were investigated. The narrow NMR signal from ice is caused by the mobile H₂O molecules on the ice/gas and ice/Teflon interface. The mobile water phase is in comparatively steady quasi-equilibrium with the strongly defective structure of the bulk ice. The relation of superficial ice properties with grain size is discussed.
- 82 47973 R Surface phenomena at ice/gas and ice/solid interfaces
V.F. Kiselev, V.I. Kvlividze, A.B. Kurzaev (USSR)
Dokl. Sovbshch.-Mezhdunar. Konf. Merzlotoved, 2nd, 1973, 4, 199-202 (Russian) Ed. by N.A. Tsytovich et al., Yakutsk, USSR
A review on the liquid-like layer on ice. A narrow signal was obtained in NMR spectrum of polycrystalline ice which showed that a mobile phase was present on ice at T below its MP. 17 ref.
- 82 47974 R Surface of ice
(X) N.H. Fletcher (U New England, Australia)
Phys. Chem. Ice, Pap. Symp. 1972 (Publ. 1973), 132-6, E. Whalley et al., ed, Roy Soc. Canada, Ottawa
A Review on theoretical and exptl studies of surface of ice which may have a quasi-liquid transition layer at T slightly below the MP.
- 82 145634 NMR of the mobile water phase on the surface of ice
V.I. Kvlividze et al (Moscow, USSR)
Vestn. Mos. Univ., Fiz. Agronomiya 1974, 15(6), 736-8
The previously expressed hypothesis (1970) that the narrow component of the NMR signal of ice corresponds to the mobile H₂O molecules on the ice surface, whereas the wide component corresponds to the mobile H₂O molecules in the ice lattice, is confirmed. The mobility of H₂O in the ice bulk is much lower than that in the subsurface layer.
- 82 158151 P Reducing the strength of ice
(X) C.F. Parks, K.H. Nimerick (Dow Chemical)
Ger. Offen 2,433,198 (1975)
Mixtures of HO(CH₂CH₂O)_nH (n=1-3) or BuOCH₂CH₂OH with polyacrylamide, gelatin, urea, hydroxyacetic acid, EDTA (ethylene-diamine tetra-acetic acid) tetra sodium salt, sodium acetate, or a similar compound were added to water which was frozen to prepare ice of low compressive strength. The mixtures were also applied to coal particles exposed to moisture and

cold to permit easy crushing of frozen masses. Thus, water containing 2.5% glycol and 0.1% polyacrylamide (30% hydrolyzed) was frozen at -18°C to give ice of compressive strength 4.2 kg/cm^2 (59.7 psi). [cf. 28 5900⁸, 52 5930¹, Sayward (1963)].

82 173871

Heterogeneous freezing nucleation in electric fields

J.B. Doolittle, G. Kali (U. Wyoming)

J. Atmos. Sci. 1975, 32(2), 375-9

Heterogeneous freezing nucleation in electric fields was studied on samples of water containing organic nuclei or AgI. Electric fields of 6000 V/cm DC were applied over sets of supercooled drops supported on a silicone varnish coated surface during different T-time sequences. In no case was a significant difference in nucleation rates observed due to the field. Electric fields of $< 6000 \text{ V/cm}$ have no intrinsic effect on the heterogeneous freezing process and the probability of enhanced ice nucleation in the atmosphere due to natural electric fields is quite remote.

83 44464

Lab studies of friction of rubber on ice

S. Venkatesh (India)

(X)

Tribol. Int. 1975, 81(2), 51-5 (English)

Lab apparatus was developed and used re frictional characteristics of rubber on ice using various parameters, such as load, speed, T, type of ice surface. The coef. of friction decreased with increased load or T, increased with rubber softener content. [cf. 78 31121, 84 45716].

83 48738

Adhesion of ice frozen from dilute electrolyte solutions

H.H.G. Jellinek (Clarkson Col.)

(X)

ACS Symp. Ser. 1975 (8), 248-60 cf. CA 83 152,928 (corr. date to 1975)

An analysis of experimental data reported by R. Smith-Johannsen (1946) on adhesion of ice frozen from dilute electrolyte solutions (NaCl , KCl , NaOAc , NaNO_3 , KOAc , NH_4Cl , CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, MgCl_2 , $\text{Th}(\text{NO}_3)_4$, $\text{Ni}(\text{NO}_3)_2$, $\text{Be}(\text{NO}_3)_2$, or KCNS) to wax-treated aluminum and clean aluminum surface at -10°C showed that adhesion strength (measured by force/cm² to shear ice off the substrate surface) was due mainly to the shearing of an interfacial liquid solution layer that formed during freezing. The thickness of such a layer is mainly proportional to the ratio of salinity of initial to salinity of saturated solution in the grain boundary. If the T of the ice-substrate system is below the eutectic point of the electrolyte, then the adhesive strength is apparently increased compared to T above the eutectic.

- 83 103763 Effect of the interphase boundary on the melting of ice in heterogeneous systems
(X) V.I. Kvlividze, A.A. Ananyan, A.V. Krasnushkin, A.B. Kurzaev (USSR)
Suyazannaya Voda Dispersnykh Sist. 1974, 3, 120-6
The properties of the interface boundary in H₂O-solid systems affects significantly the phase transitions of H₂O. Lowering the phase transition (freezing) T of H₂O in contact with a solid phase was due to liquid film at the interface. Film thickness depends on the energy of H₂O molecules interaction with the solid surface. This can explain also the MP T lowering of ice in capillaries. The concentration of the mobile phase on the surface of solids was determined by NMR as f(T) for the binary system of H₂O with solids: Aerosil, Ftoroplast, or Kaolin.
- 83 117085 Field tests of organosilicon epoxide coatings on fishing boats
(X) V.V. Panov et al (USSR)
Tr. Arkt. Antarkt. Nauchno. Issled. Inst. 1975, 317, 127-31
Coating of fishing boat superstructure with organosilicon epoxide resins decreases adhesion of ice. The decrease vs. wood or metal coated with ordinary marine paints is 2-10 times, depending on icing conditions and distance from sea water. The salinity of the formed ice decreases as distance from sea water increases.
- 83 117122 Effect of weak electric fields on the water-repellency of surfaces. Experimental data.
(X) R.T. Ebatullina, A.V. Panyushkin, E.I. Romanov et al (USSR)
Tr. Arkt. Antarkt. Nauchno-Issled. Inst. 1975, 317, 103-17
The action of AC or DC electric field on organosilicone or FHC coatings during their transition from liquid to solid state in an exptl drier caused an increase in contact angle θ between coating and H₂O. The electric current (potential) not only increased θ but also improved ability of coatings to remain hydrophobic on exposure to atmospheric conditions, water or organic solvents. The increase of θ could also be obtained by increasing the concentration of polyethylene polyamine in the coating formulation and adding pigments. The optimum drier T was 150°C for 1.5 hr. [cf. 83 165898.]
- 83 117123 Effect of the surface water-repellency on the heat transfer from this surface to the air-water spray mixture.
(X) E.A. Arrtov, V.V. Panov, A.V. Panyushkin (USSR)
Tr. Arkt. Antarkt. Nauchno-Issled. Inst. 1975, 317, 118-20
The coating of a ship's topside with a hydrophobic paint decreases the k/α ratio (k and α are resp. the heat transfer

coef. from ship's superstructure to dry air and to air depositing 5×10^{-4} kg/m²-sec water spray) and thus decreases the icing at subzero T. The uncoated flat deck has $k/\alpha=2.47$. The coated deck with the angle of wetting in the 150-170° range has $k/\alpha=1.01$. The combination of the electric superstructure heating and hydrophobic coating reduces the ice build-up to nil under most conditions. [Rationale is worded in abstract not wholly clear.]

83 165898

(X)

Effect of an electrical field on ice adhesion to the surface of perfluorinated water-repellent coating
A.V. Panyushkin et al (USSR)
Tr. Arkt. Antarkt. Nauchno-Issled. Inst. 1975, 317, 99-102
Application of a finish coat of fluorinated hydrocarbon over the epoxy resin EP-K05-ZK (56730-72-4) and hardening it in an electric field produces a surface with < 0.1 kg/cm² (1.4 psi, 0.1 atm) adhesion to ice in the -25 to 0°C range. Most pigments increase the adhesion, especially pigments with high surface energy, such as kaolin or rutile. Carbon black has relatively low energy (heat of wetting 32 ergy/cm²) and can be used in the ice repellent coatings. [cf. 83 117122].

83 208580

(X)

Heterogeneous ice nucleation in the presence of aliphatic amines and ammonia
R. Schnell, G. Vale (U. Wyoming)
US NTIS, AD-A Rep. 1974, No. 009959, 32 p.
From U.S. Gov. Rep. Announce, Index 1975, 75(15), 14
By far the most widely applied principle for deliberate modification of atmospheric precipitation processes has been creation of additional ice particles in clouds by seeding. An alternative approach is the inhibition of nucleation. There is fairly extensive evidence, mostly from lab expts, that certain vapors can significantly reduce the nucleating abilities of various nucleating materials. Nucleation inhibition processes and possibilities of applying inhibitors to natural clouds were studied, using three major exptl approaches: (1) freezing of water droplets containing known amounts of nucleants and additives, (2) activation of deposition nuclei in a static diffusion chamber, (3) field tests. [cf. 52 5061^C].

84 19402 P

(X)

Antifrost composition
M. Skabir, M.M. Derbevena, A.S. Denisova et al (USSR)
USSR 484,242 (1975)
From Otkrytka Isobret., Prom. Obraztsy, Tovarnye Znaki 1975, 52(34), 62
Compositions with low adhesion to ice consisted of silicone rubber 12.55-20.0, poly (methylsilazane) 2.5-8.4, chlorosulfated polyethylene (8002-88-4) 3.75-5.8, poly (ethylsilazane) 7.9-12.5, and Aerosil (7631-86-9) (fumed amorphous silica) 0.65-5.0 parts, with remainder being solvent.

84 45716

Friction of rubber on ice

E. Southern, R.W. Walker (Malaya Rubber..., England)
Am. Chem. Soc. Div. Org. Coat. Plast. Chem., Paper 1974,
34(1), 982-9

(X)

At low sliding speeds, friction of natural, neoprene and SBR rubbers on ice, and similarly on other smooth surfaces, is determined by the viscoelastic properties of the rubber. Increasing the load, or contact pressure, decreases the friction coef. in accord with theory that the true contact area depends on contact pressure. Carbon black-filled rubbers exhibit this viscoelastic behavior but the changes in frictional coef. are not analogous to changes in dynamic properties. Frictional melting of the ice surface sharply decreases the friction coef. at high sliding speeds.

84 50280

Adhesion of ice to the surface of quartz capillaries

O.A. Kiselya, S.N. Klad'ko, V.D. Sobolov, N.V. Churaev (USSR)
Kolloidn. Zh. 1975, 57(6), 1220-2

(X)

A method is described for studying adhesion of ice to the surface of quartz capillaries (radius 10-15 μ) based on observation of displacement of the ice column caused by application of gas pressure. Adhesion decreases abruptly at -4 to -6°C for moisture in pores in concrete and at -3.5°C for pure water. The decrease in adhesion is caused by formation of a liquid phase interlayer between ice and capillary surface.

84 65146

Effect of temperature and water salinity on ice adhesion to structural materials and coating

A.V. Panyushkin, N.A. Sergaheva, Z.I. Shvaishtein (USSR)
Tr. Arkt. Antarkt. Nauchno-Issled. Inst. 1975, 317 75-9
Lab studies showed that the physical-chemical features of the base and chemical composition were the main factors influencing the strength of ice adhesion. Adhesion of ice formed from artificial sea water was 20-35% of that of ice formed from distilled water. Decrease in T of ice formation from 0 to -30° increased adhesion strength by 20-40%.

(X)

84 124689

A numerical investigation of the efficiency with which simple columnar ice crystals collide with supercooled water drops

R.J. Schlamp, H.R. Pruppacher, A.E. Hamielac (UCLA)
J. Atmos. Sci. 1975, 32(12), 2330-7

(X)

Theoretical derivations and calculations were applied... For -8°C and 800 mbar, the trajectory of drops relative to a cylinder was calculated by a semi-empirical method. From the trajectory of water drops relative to columnar ice crystals, collision efficiencies were computed. Results predict riming on a column crystal will not occur until crystal has dia. >50 μ (0.05 mm, .002 in.). This result agrees with field observations in the literature. [Would a razor edge help avoid ice build-up, e.g. on a wing or rotors? JMS 6/23/77].

84 143292

(X)

Volta effect and liquid-like layer at the ice surface
E. Mazzeza, U. Del Pennino, A. Loris, S. Mantovani (Italy)
J. Chem. Phys. 1976, 65(3), 1028-32

The Volta potential difference between Ih ice single crystals and different metals was measured as $f(T)$ by the vibrating electrode technique. Reproducible results were obtained with ice/gold and ice/copper contacts, indicating that in these cases the equilibrium was obtained. Below -30°C the dependence is linear, and this is the effect of the impurity content on the ice Fermi level. At higher T a term which is logarithmic in $(T - T_m)$, where T_m is MP of ice, is added. This additional potential difference has proved to be localized at the ice surface and ranges 0-150 mV; it can be directly related to the appearance and thickening of the polarized, liquid-like layer predicted by N.H. Fletcher (1973), if it is assumed that a constant electric field exists in the layer interior. The preferred dipole orientation turns out to be that with the 0 outwards. An approx. value of 4.3 eV was obtained for the ice work function.

[If indeed the 0 atoms tend to be outward, one can see how H-bonding to a substrate can be a factor in ice adhesion, and how adhesion is less when the substrate is free of H-bonding capability, as for hydrocarbons, fluorocarbons, etc. JMS 1/27/78.]

85 80247

Effect of the surface tension of liquids on the adhesion of an air bubble to the surface of solid substances

F. Dedek, M. Barcal

Acta. Mont. 1975, 36, 35-46 (Czech.)

Kinetics and conditions of adhesion of air bubbles to surfaces of solid particles are essential factors in flotation. They are influenced primarily by surface tension of water, bubble velocity at instant of contact, and solid surface properties. Experimented with air bubbles expelled toward submerged pre-treated hard paraffin. Bubbles adhered on first or second contact, depending on nature and concentration of surfactant and bubble speed. Good results obtained with n-heptanol even at low concentration.

85 127550

Experimental study of adhesion of ice under lab and natural conditions

V.V. Panov et al.

tr. Arkt. Antarkt. Nauchno-Issled. Inst. 1975, 326, 147-154 (Russ.)

Effects of substrate free energy, substrate surface relief, thermodynamic parameters characterizing the formation of adhesive contact, supercooling, freezing T , H_2O chemical composition and number of freeze/melt cycles on the adhesive forces were measured on a self-constructed apparatus. Semiempirical relations for calculation of adhesive forces and the effect on them of T and salt content are presented.

85 194169

Study of the adhesion of ice to structural materials, anti-corrosion and anti-icing coatings

A.G. Tkachev et al

Kholod. Tekh. 1976, (80, 15-18 (Russ.))

The adhesion of ice to structural materials and coatings depends primarily on physicochemical and mechanical properties of the coating, chemical constitution of the water, and freezing T. The metallic surface of cooling apparatus can be protected against corrosion by organosilicate anti-icing OSM coatings. These coatings also reduced the adhesion of ice to steel surfaces to 1/2 to 1/5 of original value.

86 96504

Contact angle and hysteresis, with some reference to flotation research

I.W. Wark

Aust. J. Chem. 1977, 30(1), 205-9

A technique used in flotation research for contact angle measurement is recommended for wider use. The effect of one aspect of surface roughness on the relative motion of fluid/solid systems is discussed. The function of the water vapor in the gas phase adjacent to the line of triple contact is examined. A claim of the Russian school of surface chemists is questioned, namely, that a discrete film of H₂O on the solid surface invariably dominates both hysteresis and contact angle.

86 177930

Stability and dynamics of a droplet on the surface of a solid

V.S. Yushchenko et al

Kolloidn. Zh 1977, 39(2), 335-8 (Russ.)

A model of 2-dimensional microdroplets on a structureless adsorbing substrate is described. A macroscopic approach can be used for description of microheterogeneous systems in which the dimensions of the bodies studied are nearly molecular. The statistical concept of contact angle at the molecular level was established. Various microstates and processes at molecular level corresponding to an equilibrium macrostate and macroscopic processes were analyzed.

86 177961

A new method of determining contact angle by a sessile drop upon a horizontal surface (sessile drop contact angle)

D.J. Ryley, B.H. Khoshalm

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Contact angle is measured by magnified projected image of a sessile drop, assuming the profile elliptical, and finding Cartesian coordinates of selected points on the profile. By selecting groups of three such, the mean equation to the outline can be determined and thus the tangent at the observed point of contact. The method was tested with H₂O drops on steel and Hg drops on glass. Results agreed with data obtained by tilting plate method and with those of other

investigators who used analytical methods to define drop shape. If the sessile drop is assumed to be a part-oblate spheroid, a minimum free energy analysis illuminates several experimentally observed features of its shape.

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On deviations from Young's equation

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Young's equation for surface tension of liquid drops at the air-solid interface is discussed in terms of macro and microscopic contact angle; the latter, θ being the angle between the free liquid surface and the solid substrate at liquid thickness $\ll 10$ Å, i.e. microscopic near the 3-phase contact line. The macroscopic θ^c given by Young's equation is shown to be the angle between the liquid surface and the substrate at microscopically large distance from the contact line where the modification of surface tension by interaction is negligible (>10 Å). The connection between θ^p and θ^c is established by making only general statements about the nature of this interaction and does not impose on the profile shape in the neighborhood of the 3-phase contact line the unphysical restrictions which lead to the conclusions of G.J. Jameson and M.C.G. del Cerro (1976).